Development of an Atmospheric Mercury Modeling System for the Great Lakes Region

Final Report to the United States Environmental Protection Agency from the Wisconsin Department of Natural Resources

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In September 2001, the Wisconsin Department of Natural Resources received a grant from USEPA under the s.105 Great Lakes geographic initiative to help fund the development of an atmospheric mercury modeling system for the Great Lakes region. This document and associated data results represent the final report to USEPA and serve to fulfill the Departments obligation under the USEPA grant agreement.

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I. Introduction

Atmospheric deposition of toxic compounds, such as mercury, into lakes and streams is known to have adverse effects on water quality and fish life. When mercury (Hg) is deposited on the surface of water bodies it can become methylated and bioaccumulate in fish. Human population and wildlife that consume sufficient quantities of fish may be exposed to mercury levels that are harmful to their health. As a result of this deposition the Wisconsin Department of Natural Resources (WDNR) issues annual fish consumption advisories for all Wisconsin waters.

Because of the fish consumption advisories and mercury rule development the WDNR needs the ability to model atmospheric mercury and its deposition. In light of this need, the WDNR worked with ENVIRON and Atmospheric & Environmental Research (AER) to test new model code which has been modified to include Hg chemistry. The base model used for this mercury modeling study was the Comprehensive Air Quality Model with extensions (CAMx). Modifications to the code included the addition of a new chemistry module for Hg to treat the gas- and aqueous-phase chemistry of Hg species. After developing the new code, ENVIRON modeled the entire year of 2002. This was done to highlight the seasonal cycles in mercury deposition.

Subsequently, the WDNR used the CAMx model to study an episodic event to determine the importance of convective rainfall to Hg deposition. WDNR analysis indicates that summertime precipitation has a higher concentration of mercury than the other seasons. The analysis also indicates that a disproportionate amount of the deposition occurs with high rainfall events. Thus, understanding the role of convection in summertime rainfall events is critical to understanding mercury deposition.

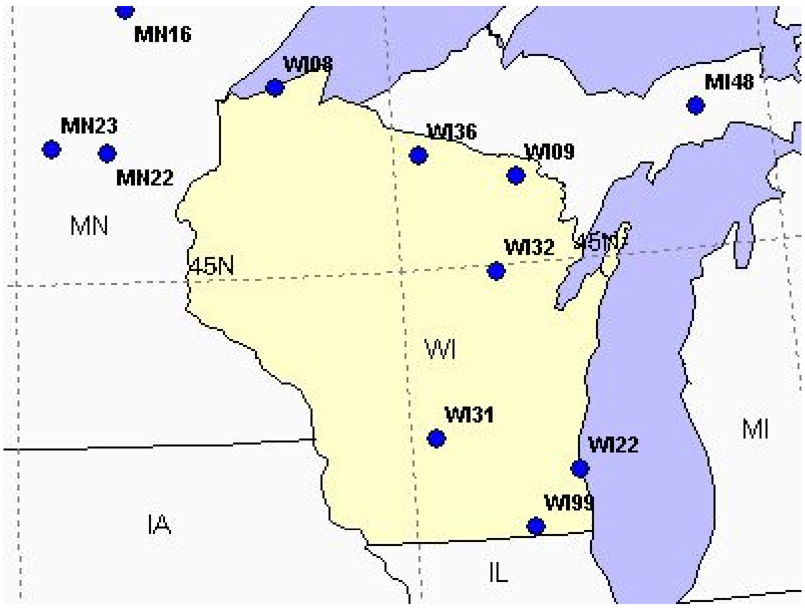
II. Data Analysis

A) Observed Mercury Deposition Data

Rainfall or snow samples (mm) from the MDN sites in Wisconsin (Figure 2-1) are lab-analyzed for concentrations of total Hg (ng/L). These concentrations of Hg in the precipitation consist almost completely of divalent, reactive mercury, Hg(II), which is water soluble. Particulate Hg, Hg(p), are removed from the atmosphere by dry deposition processes (Keeler, Glinson, & Pirrone, 1995) and do not figure into wet deposition activity. Traces of gaseous non-reactive, non-water soluble elemental mercury, Hg(0), are also in these precipitation samples (Seigneur, Karamchandani, Vijayaraghavan, Lohman, & Yellru, 2003). Consequently, the MDN mercury measurements are collectively referred to as “precipitation Hg”. Each MDN wet deposition estimate (ng/m^2) is derived simply by multiplying each sample’s precipitation amount by the measured precipitation Hg concentration in that water volume.

B) Physical processes that influence Hg wet deposition

Figure 2-1. Wisconsin MDN site map



Site	Name
WI08	Brule River
WI09	Popple River
WI22	Milwaukee
WI31	Devil's Lake
WI32	Middle Village
WI36	Trout Lake
WI99	Lake Geneva

Note: (NADP, n.d.)

Hg(II) is the predominant Hg specie in wet deposition processes yet Hg(II) typically constitutes less than 3-5% of the airborne Hg mass, which is largely comprised of Hg(0) (Lindberg & Stratton, 1998).

Estimates of MDN weekly Hg wet deposition amounts are affected by several complex, inter-related factors: a) location of the monitor relative to upwind source regions of Hg, b) the distribution of atmospheric Hg, (especially Hg(II)) in the air advected towards the MDN site and subject to wet removal from rainout, c) competition with dry deposition processes for removal of Hg (Pai, Karamchandani, & Seigneur, 1999), d) pre-rain meteorological features: advection and convection patterns, moisture availability, the atmosphere's capacity to hold the moisture in the vapor state, and e) the varying temporal, spatial, intensity and duration characteristics of each precipitation event during the sampling period.

To complicate matters further, it is possible that up to several precipitation events can impact an MDN site during any week, with each occurrence potentially transporting air from a different source region. Additionally, Hg(II) can also be removed by dry deposition processes, which can affect its availability for wet scavenging.

Seigneur et al. (2003) reviewed recent MDN data throughout the eastern half of the United States. They found some of the spatial patterns in the data to be so complicated that they were labeled as being counter-intuitive. These confounding MDN data had Seigneur et al. (2003) asking why Hg wet deposition fluxes in remote northern Minnesota were greater than in northern

New York and many areas of Pennsylvania. These latter two states are immediately downwind of significant sources of atmospheric Hg (power plant operations and other major anthropogenic activity).

Scavenging and removal rates for atmospheric Hg in single rain events can be further complicated by any continual advection of significant amounts of atmospheric Hg, particularly Hg(II), to the site area during the rain episode. Variations in Hg airborne residence times, air path trajectories, and atmospheric mixing also need to be addressed in estimating the range of Hg precipitation concentrations in the MDN samples. Seigneur et al. (2003) point out that Hg(0) can remain airborne for several months, sometimes up to a year, while Hg(II) has much shorter atmospheric residence times.

Seigneur et al. (2003) further state that airborne mercury has the potential to be subject to any of the following atmospheric chemistry processes: a) some Hg(0) can undergo either aqueous-phase or gas-phase oxidation to yield Hg(II), b) some Hg(II) are capable of gas phase reduction to Hg(0), and c) some of the Hg(II) can also be adsorbed onto particulate matter. How these transformation processes interact can affect the atmospheric lifetimes of the Hg species and, consequently, Hg removal and wet deposition rates.

Seigneur et al. (2003) note that different cloud types also have the potential to affect the efficiencies in Hg rainout (in-cloud scavenging) and washout (below-cloud scavenging). They state that stratiform clouds yield precipitation with little updraft, which makes washout predominate. Conversely, cumuliform clouds with strong updrafts should yield more rainout.

Seinfeld and Pandis (1998) developed a general conceptual model that attempted to inter-relate the numerous physical processes that can contribute to the wet deposition of pollutants in the troposphere (Figure 2-2). Most of the processes identified in this diagram pertain to the wet deposition of Hg and gives a general appreciation for the considerable complexity involved in the wet removal of air pollutants, including Hg, from the atmosphere.

C) Wisconsin MDN data during December 1995 through December 2002

The distribution of 1261 site-weekly MDN precipitation Hg concentrations in Wisconsin during December 1995 – December 2002 as a function of increasing site-weekly precipitation amounts (0.4 mm bins) is graphed in Figure 2-3. This display reveals that there appears to be no discernible relationship between weekly precipitation totals and the Hg content in them, at least at MDN sites in Wisconsin.

Figure 2-2. Conceptual framework for wet deposition processes

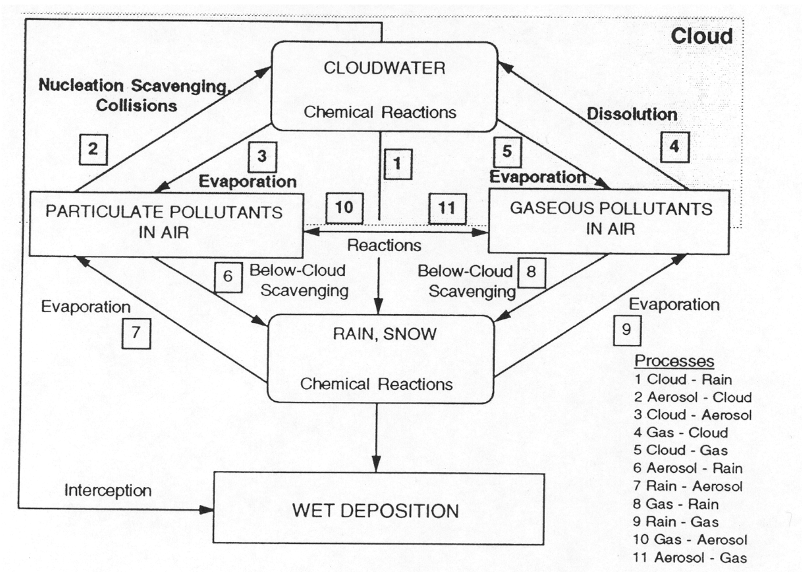
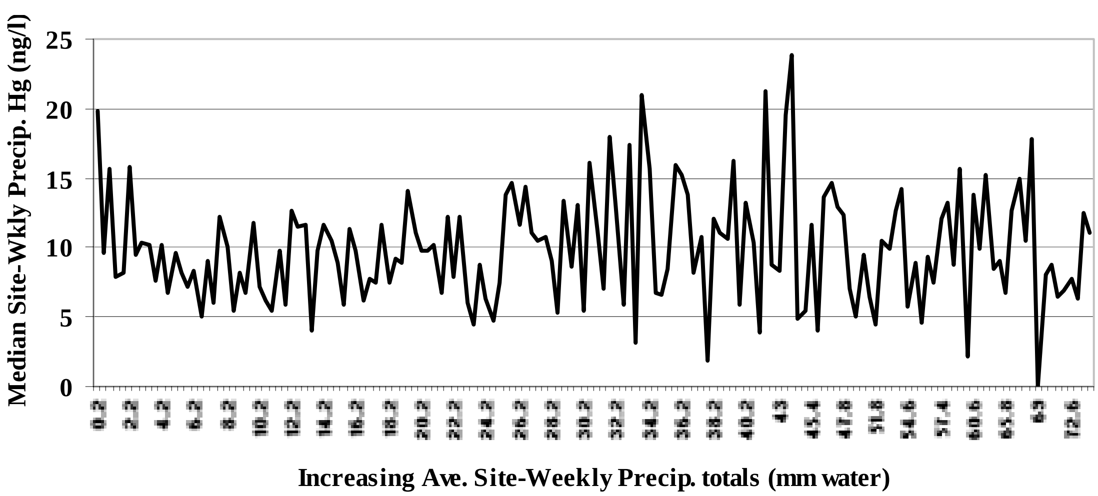


Figure 2-3. Median site-weekly precipitation Hg concentrations vs. increasing site-weekly precipitation. Wisconsin MDN sites, December 1995 - December 2002



There does appear to be a semi-annual cycle in median weekly values for both measured precipitation Hg (Figure 2-4) and derived Hg wet deposition totals (Figure 2-5) for those four Wisconsin MDN sites that fully operated during 1996 – 2002. Mercury levels during precipitation events were significantly higher during the "warm" months of mid-April to mid-October, compared to the relatively "colder" months of mid-October to mid-April. Possible explanations of this sizable difference in wet Hg levels between these six month periods include snow noticeably reducing the scavenging and removal efficiencies relative to liquid water and the possibility of less atmospheric Hg in Wisconsin during October-April due to a reduction in anthropogenic activities that generate airborne Hg (primarily electrical generation) and northerly wind patterns in Wisconsin advecting air from cleaner areas (Moran and Hopkins, 2002). This speculation needs to be further investigated.

Figure 2-4. Median precipitation mercury concentrations for 26 weekly sampling periods, 1996-2002 at four Wisconsin MDN sites

(Brule River W108, Popple River W109, Trout Lake W132, and Lake Geneva W199)

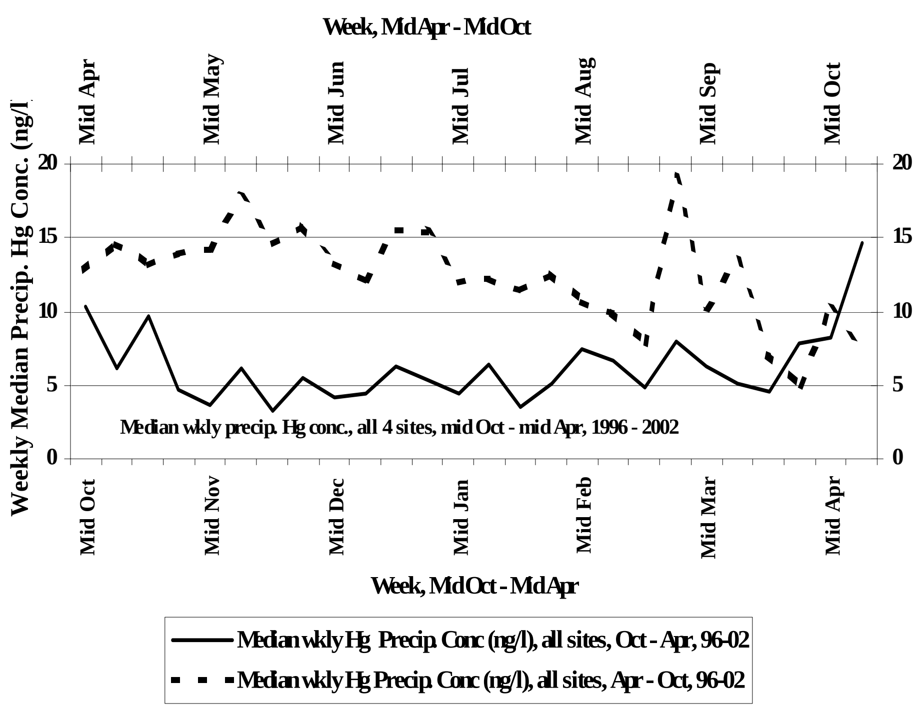
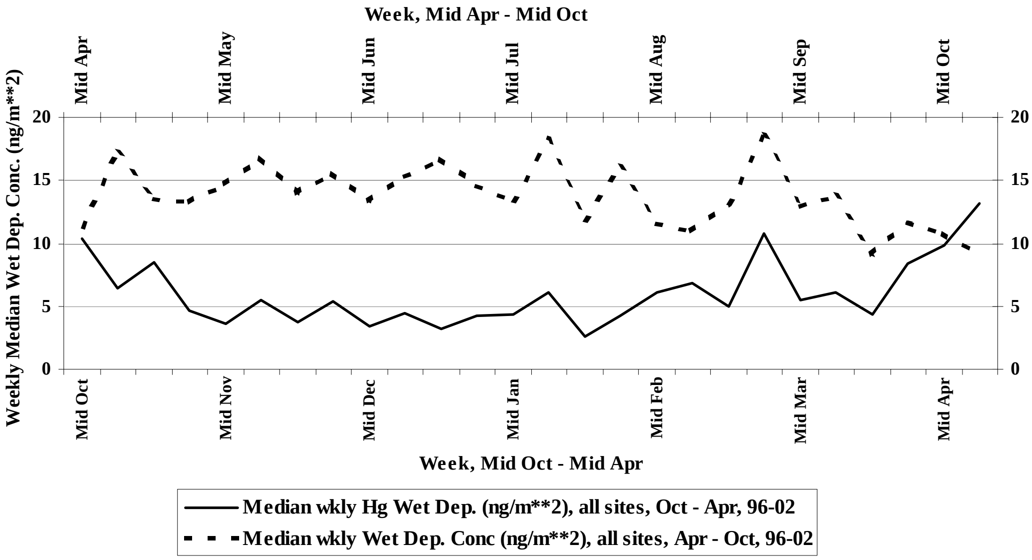


Figure 2-5. Median mercury wet deposition concentrations for 26 weekly sampling periods, 1996-2002 at four Wisconsin MDN sites

(Brule River W108, Popple River W109, Trout Lake W132, and Lake Geneva W199)



D) Wisconsin region MDN data during April 16 – 23, 2002

For this study, the potential for considerable variability in both precipitation rates and resultant Hg precipitation levels are evident by looking at the event-based (not weekly) measurements at the Devils Lake MDN site during the week of April 15–22,2002 (Table 2-1). During the first sampling period (April 15-17), only 1.3 mm of rainfall was recorded at the site. The Hg content in this precipitation was 32.6 ng/L. The next measurement (April 17-18) measured 35.6 mm of rain, a 2740% increase over the previous time interval. However, there was only 23.2 ng/L of precipitation Hg in that sample, a 29% decline from that for the previous sample.

Table 2-1. Devil's Lake precipitation measurements for April 15-22, 2002

Measurement Interval	Total Precipitation (mm)	Hg Precipitation Concentration (ng/L)
April 15-17, 2002	1.3	32.6
April 17-18, 2002	35.6	23.2
April 18-19, 2002	5.6	28.1
April 19-22, 2002	13.6	7.5

The substantial range in rain vs. precipitation Hg suggests that during relatively heavier, more sustained rain events, most of the mercury present in the atmosphere is scavenged out during the initial portion of the event. It is reasonable to speculate that subsequent precipitation has less airborne Hg available for wet removal.

The precipitation during Devils Lake's final rain event (April 19-22) of the episode had relatively little Hg content (7.5 Hg ng/L). This implies that minimal atmospheric Hg was advected into the Devils Lake area after the convective activity of the previous days.
The absence of a correlation between rainfall and Hg deposition at Devil's Lake supports the possibility that even over longer periods of time and larger geographical areas rainfall and Hg deposition are not correlated.(Figure 2-3).

The relatively high percentile ranks for the weekly Wisconsin MDN data of April 16-23, 2002, (Table 2-2) indicate that there was a considerable loading of atmospheric Hg, particularly Hg(II), available for wet scavenging at these locations during this period. It can be reasonably estimated that the sizable amounts of precipitation Hg during this week means that much of the atmosphere over Wisconsin (and adjacent states) contained relatively high levels of Hg during this period that were available for wet removal.

Table 2.2. Measured and percentile ranks of total precipitation and Hg concentration at Wisconsin MDN sites for April 16-23, 2002

MDN Site	Total Precipitation (mm)	Total Precipitation (percentile rank)[b]	Hg Precipitation Concentration (ng/L)	Hg Concentration (percentile rank)[b]
Brule River WI08	19.6	74.4%	21.4	84.5%
Popple River WI09	66.4	98.7%	17.5	82.1%
Trout Lake WI36	42.2	90.5%	21.2	91.4%
Lake Geneva WI99	25.7	73.0%	42.9	96.3%
Middle Village WI32	8.4	33.3%	2834	94.9%
Devil's Lake WI31	56.1[a]	N/A	91.4[a]	N/A

[a] Devil's Lake MDN: The sum of data from four sequential periods covering April 15-22, 2002 was used to calculate precipitation.
[b] Percentile rank among each site's total distribution of weekl measurements, 1995-2002.

MDN data for sites in the states adjacent to Wisconsin for the same week show a similar pattern (Table 2-3). The data reflect a wide range in the measured rainfall and the precipitation Hg. These data strongly suggest that widespread advection, convection, precipitation and deposition processes on a synoptic scale were favorable in yielding considerable Hg wet deposition throughout the region during the rain events of April 16-23, 2002.

Table 2-3. Measured total precipitation and Hg concentration at Midwest MDN sites for April 16-23, 2002

MDN Site	Total Precipitation (mm)	Hg Concentration (ng/L)
Fernberg MN18	8.1	15.5
Marcell MN16	9.7	40.0
Camp Riley MN23	21.8	27.1
Lamberton MN27	16.0	17.3
Indiana Dunes IN34	37.8	23.8
Bondville IL11	23.7	11.5

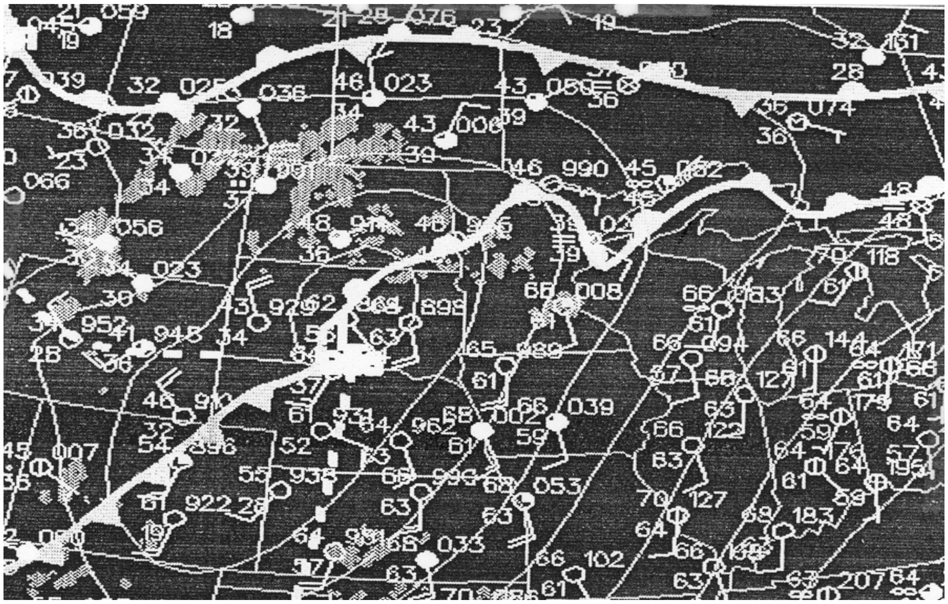
E) Meteorology and rainfall during April 16 – 23, 2002

Rainfall events are the main source of the Hg measured at MDN sites. Unfortunately, almost all of the MDN sites collect and analyze precipitation samples on a weekly basis. This is a rather long time scale when assessing the influence of rain events that have lifetimes of as short as several minutes. Since precipitation typically occurs only during a small fraction of each week at a site, it can be difficult to ascertain the characteristics of those individual precipitation events when the airborne Hg is impacting the sampler as part of the rain.

A review of daily archived synoptic weather charts, temperature and precipitation measurements from NWS stations in the Wisconsin area during April 16-23, 2002, can help narrow down the timing and spatial extent of those weather features that resulted in high wet deposition of Hg during this period.

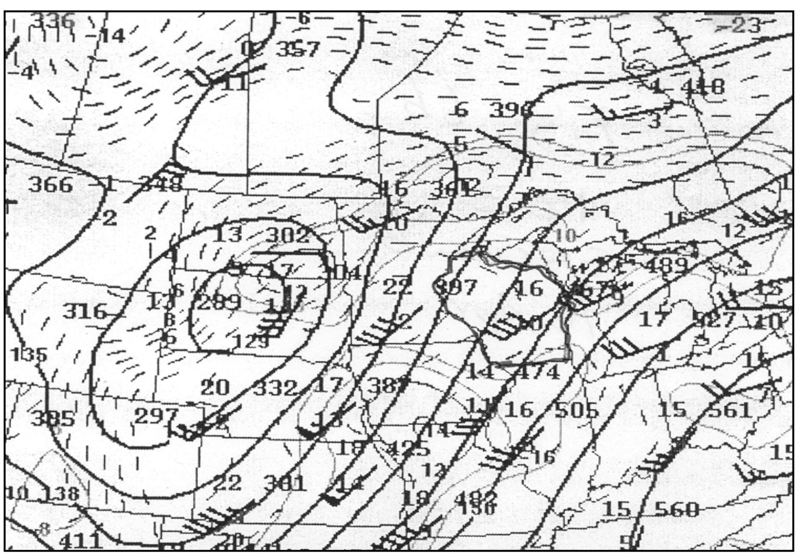
The MDN weekly sampling period being modeled commenced on Tuesday, April 16, 2002. During this day Wisconsin was on the back side of a surface high pressure system centered in the eastern US (Figure 2-6), resulting in the advection of warm, humid air into the region from the Gulf of Mexico region at the 850 mb level (about 1 mile above mean sea level), (Figure 2-7). This resulted in the region experiencing warm temperatures with maximums in the low-to-mid 80s ^{o}F (National Weather Service [NWS], n.d.). Additionally, a warm front stalled along the northern border of Wisconsin on this day (Figure 2-6). This front, which was associated with a low pressure system in the South Dakota-Minnesota region, produced some weak convective activity in northern Wisconsin, yielding clouds and scattered, light precipitation, mostly less than 4 mm (NWS, n.d.).

Figure 2-6. Central USA synoptic weather map. 7AM CDT. April 16, 2002



Note: Retrieved April 1, 2004, from http://weather.unisys.com/

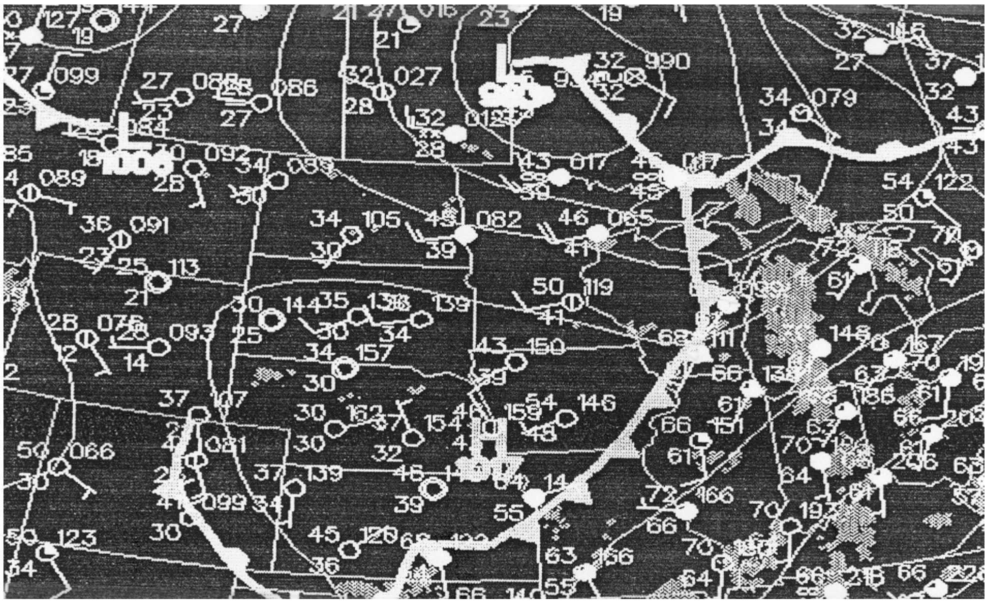
Figure 2-7. Central USA, 850 mb contour and winds map. 7AM CDT. April 16, 2002



Note: Retrieved April 1, 2004, from http://weather.unisys.com/

By April 17, 2002 a cold front associated with the low pressure system from the previous day had pushed eastward through Wisconsin (Figure 2-8). This front helped trigger some variable scattered rainfall throughout northern Wisconsin. Pertinent to the Lake Geneva and Devils Lake MDN sites, both Madison and Milwaukee reported zero precipitation during April 17th (Figure 2-9).

Figure 2-8. Upper central USA synoptic weather map. 7AM CDT. April 17, 2002



Note: Retrieved April 1, 2004, from http://weather.unisys.com/

On April 18th a different surface low pressure system and associated warm and cold fronts had moved eastward into the Minnesota-Wisconsin region (Figure 2-10). The spatial extent of the radar echos throughout most of Wisconsin (noted by grayish patches in Figure 2-10) suggest that the depth and intensity of the convection during this day in much of Wisconsin was significantly higher than during 17 April (Figure 2-8). This might help explain that 18 April was substantially the wettest day of the 16-23 April 02 period for most NWS stations in Wisconsin (Figure 2-9, e.g., Rice Lake: 20.0 mm, Antigo: 18.03 mm, Mosinee: 20.32 mm, Woodruff: 19.8 mm, Madison: 9.91 mm, Milwaukee: 9.65 mm, Rhinelander: 98.6 mm).

On April 19th the cold front had moved east into Michigan and that Wisconsin was positioned on the front end of a high pressure system centered in northern Canada (Figure 2-11). The strong northerly advection of cold air (Figure 2-12) resulted in peak daily temperatures of only mid-40’s to low 60s °F throughout the State, a decrease of 20-30 °F from the previous day (NWS, n.d.). Being dominated by a stable high pressure system, almost no rain was measured at NWS stations in Wisconsin (Figure 2-9).

The high pressure system suppressed almost all rain activity in Wisconsin on April 20th (Figure 2-13) and the remaining days of the modeling episode (NWS, 2002).

Figure 2-9. National Weather Service 24-hour precipitation totals (mm) for April 17-19, 2002

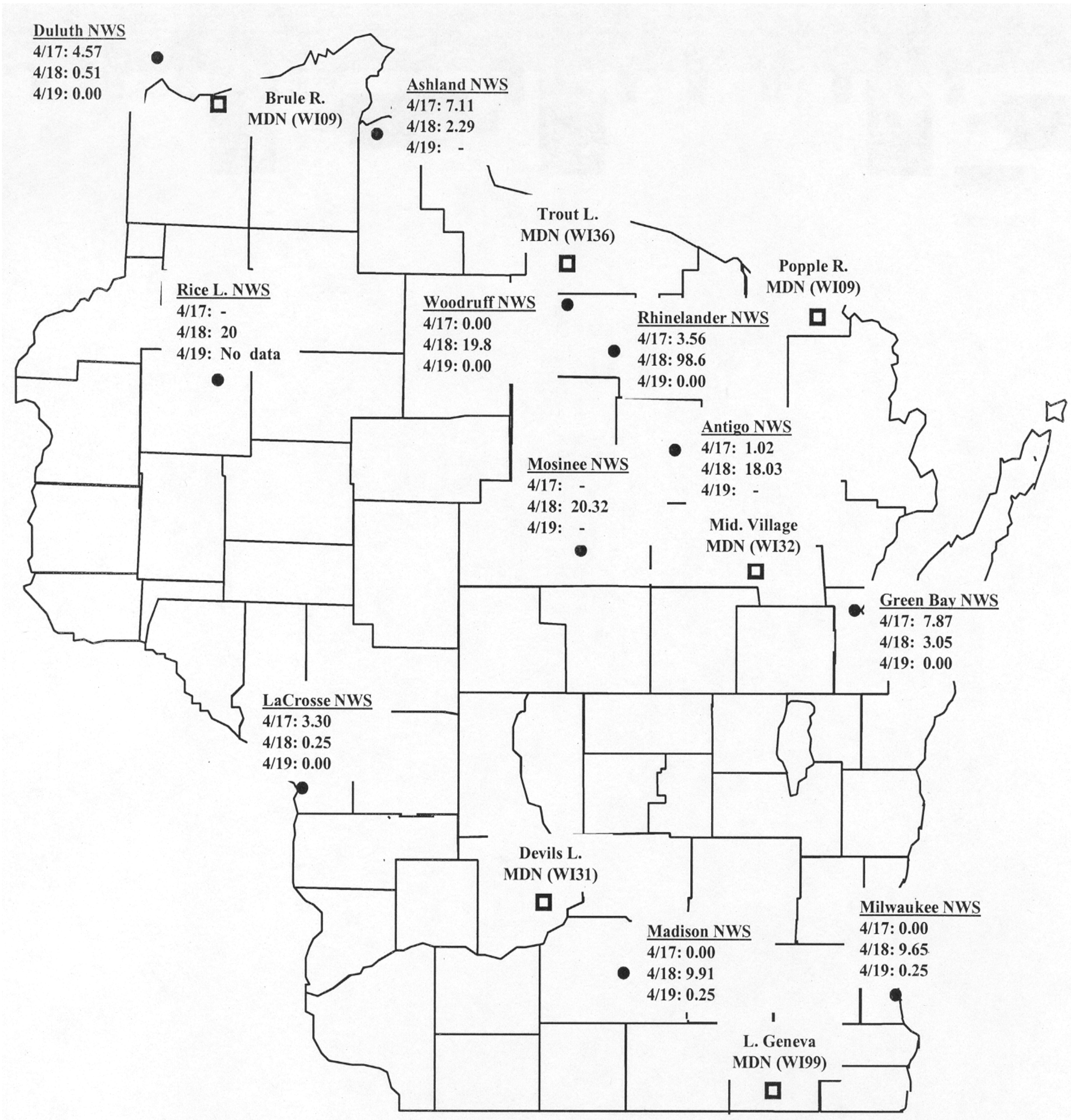
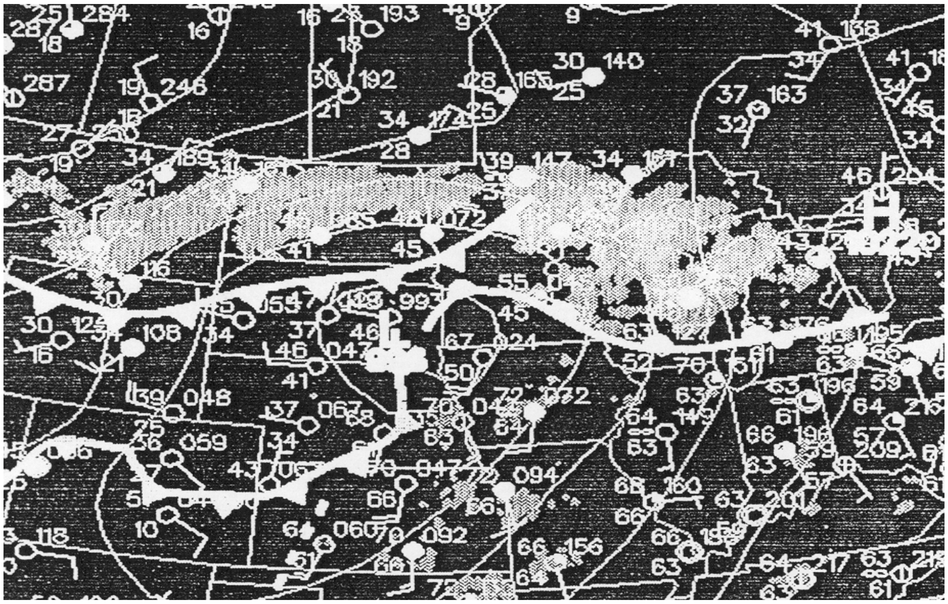
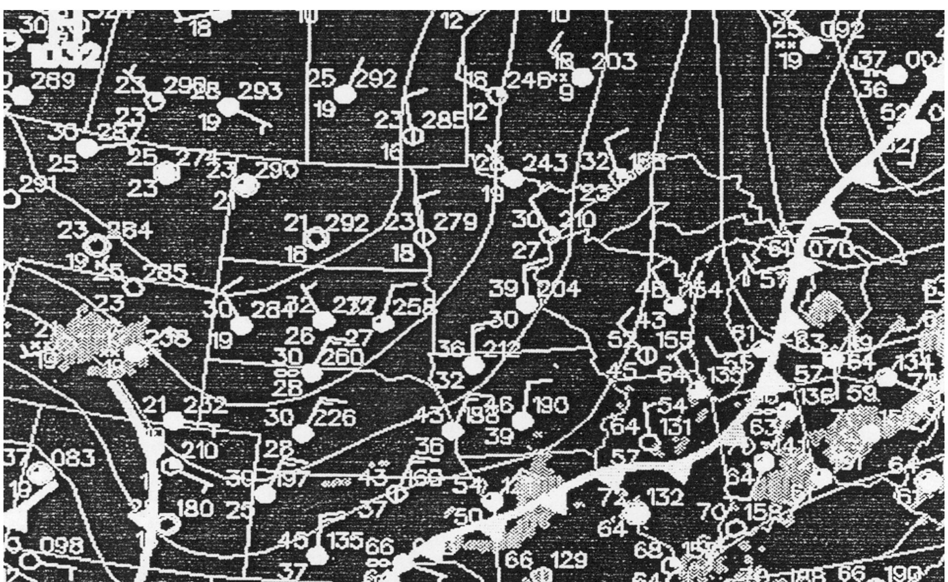


Figure 2-10. Upper central USA synoptic weather map. 7AM CDT. April 18, 2002



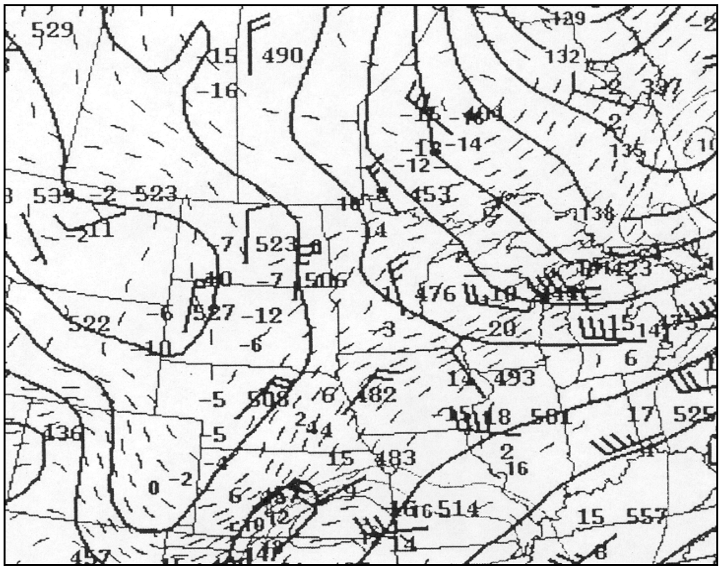
Note: Retrieved April 1, 2004, from http://weather.unisys.com/

Figure 2-11. Upper central USA synoptic weather map. 7AM CDT. April 19, 2002



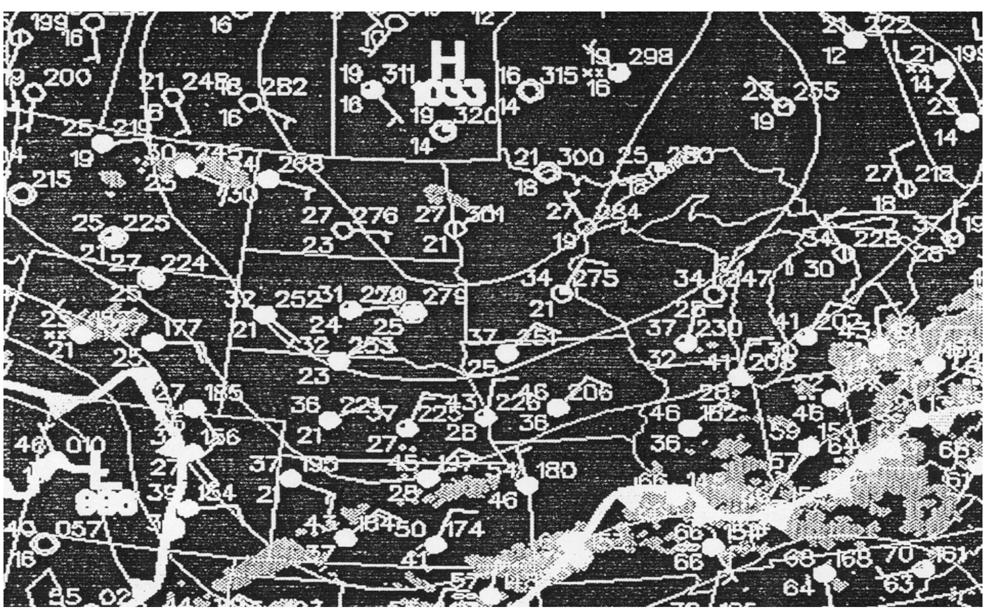
Note: Retrieved April 1, 2004, from http://weather.unisys.com/

Figure 2-12. Central USA 850 mb contour and winds map. 7AM CDT. April 19, 2002



Note: Retrieved April 1, 2004, from http://weather.unisys.com/

Figure 2-13. Central USA synoptic weather map. 7AM CDT. April 20, 2002



Note: Retrieved April 1, 2004, from http://weather.unisys.com/

F) Air parcel trajectories during April 17-18, 2002

A review of the NWS's archived synoptic weather maps and precipitation data indicate that the majority of the Wisconsin rainfall for the week of April 16-23, 2002 occurred during April 18th , with lesser amounts during April 17th (Figure 2-9). Furthermore, as previously discussed, the amount of atmospheric Hg collectively wet scavenged to the surface at the Wisconsin MDN sites during these rain events was relatively very high (Table 2-2). Consequently, it appears that there were substantial Hg concentrations aloft during the rain events that occurred near Wisconsin MDN sites during April 17-18, 2002.

These MDN sites, with the possible exception of the Devil's Lake monitor, are located in areas that are sufficiently distant from any significant Hg sources that could impact them directly. It is reasonable to assume that almost all of the Hg that was wet deposited to these sites during April 17-18, 2002 originated from upwind Hg sources relatively far away. The CAMx model uses Hg emissions data and simulated meteorological data to model the impact of these Hg sources on Wisconsin, including at the MDN sites during these days.

Air parcel back trajectories are used in an attempt to identify potential source-receptor relationships for the Hg wet-deposited at the Wisconsin MDN sites during April 17-18, 2002. The trajectory model used to simulate these back trajectories is called the HYbrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPLIT), which was originally developed and is still managed by the Air Resources Laboratory (ARL). Access to the model is available at http://www.arl.noaa.gov/ready/hysplit4.html.

As with most trajectory models, HYSPLIT assumes a steady-state (Lagrangian) atmosphere, which maintains its features, including flow, uniformly for each periodic averaging time (usually an hour) over the course of the trajectory lifetime. Consequently, the air parcel trajectory represents a series of connected pathways with the fluid parcel not varying with time. (Glickman, 2001). Because trajectories lack a time derivative (Glickman, 2001), they do not represent true atmospheric motion; however, they offer reasonable estimates of where air parcels originate (back trajectories) or terminate (forward trajectories) .

For this study, the most recent on-line version, HYSPLIT 4.7, was applied interactively via the internet. The wind data input to HYSPLIT are from the Eta Data Assimilation System (EDAS) files. These archived data are the gridded wind fields derived from applying the Eta hydrometeorological prediction model to upper air measurements collected across the US twice daily.

In modeling trajectories, accuracy diminishes as time and distance increase. Furthermore, the dominant Hg species in wet deposition, Hg(II), has an atmospheric residence time on the order of hours to days (Moore, 2002). Applying a simplified (i.e. steady-state) atmospheric model to data representing substantial convective activity (i.e., the rainfall events) challenges the abilities of HYSPLIT. Consequently, it was determined that calculating 3-dimensional HYSPLIT back trajectories of 48 hour duration offered a reasonable compromise between accuracy and identification of potential source regions for the Hg that impacted the MDN sites.

The end points for the trajectories are the latitude/longitude positions for selected Wisconsin MDN sites (Figure 2-1). The HYSPLIT runs are set up to calculate back trajectories at 3 intervals above ground level (agl); 500 m, 1000 m, and 1500m. These heights represent a reasonable array of the different altitudes where synoptic flow would be advecting Hg-laden air. Because of the complicated flow fields during April 17-18 created by the frontal activity (Figures 2-8 and 2-10]), the trajectory patterns could be quite different between 500m, 1000 m and 1500m. 48 hour back trajectories are calculated for each MDN site for April 17-18, 2002. End times are selected to capture the 24 hour period when most of the rain impacted at the Wisconsin MDN sites.

For April 17th the HYSPLIT-estimated air flow coming into Wisconsin MDN areas had a generally eastward path in mid-day (Figures 2-14 through 2-19). According to HYSPLIT calculations for a 48 hour back trajectory, these air parcels originate in the largely pristine Rocky Mountains region (1000m and 1500m agl) and southwestern or western deserts (500m agl). These air parcels then gradually converge and advect across the northern plains area into Wisconsin. One exception to this pattern occurs on April 17th in the back trajectory from Lake Geneva. For this site, the air parcel originates mostly in the Texas Gulf region.

Twenty-four hours later the predicted trajectory patterns for all six Wisconsin MDN sites had shifted to a more northeastward movement, starting in southern Texas or the Gulf of Mexico (Figures 2-20 through 2-25).

There are significant limits in attempting to evaluate these HYSPLIT trajectories in the context of Hg wet deposition at Wisconsin MDN sites. Becaues the sampling interval at Devil's Lake is based on precipitation events the rate of Hg wet removal at this site can be calculated. For the other sites the rates are unknown. The Hg emissions inventories in the general upwind sectors are unknown. And, finally, the scales and types of atmospheric Hg chemistry carried out along these pathways is unknown. Consequently, it is very tenuous to attempt estimating any type of Hg source-receptor relationships based on Figures 2-14 through 2-15.

However, it is known that the large majority of atmospheric Hg that was wet deposited at the Devil's Lake MDN site occurred during April 17-18, 2002 (Table 2-1). Based solely on the Devils Lake data, it appears that atmospheric Hg loading was much greater along the trajectory during the 48 hour period that ended at 1 PM Central Daylight Time (CDT) April 18th (Figure 2-24) than 24 hours earlier (Figure 2-18). The latter pathway had air that passed over or near several large metropolitan areas (Houston, San Antonio and Dallas TX, Oklahoma City, OK, Kansas City, MO-KS). These large cities can reasonably be considered to be sizable sources for Hg emissions, particularly from their numerous coal-fired power production facilities.

HYSPLIT-derived 48 hour back trajectories for the other MDN sites in Wisconsin for 1 PM CDT April 18, 2002 strongly resemble that for Devil's Lake (Figures 2-20 through 2-25). Consequently, it is possible that the air advecting into the Wisconsin area during much of April 18, 2002, contained relatively high levels of atmospheric Hg that originated in several major urban areas in the southern plains states. The subsequent convective activity resulted in much of this airborne Hg being wet scavenged out of the atmosphere in Wisconsin and adjacent states.

Figure 2-14. HYSPLIT 48 hr back trajectory for Brule River MDN at 1 PM CDT, April 17, 2002

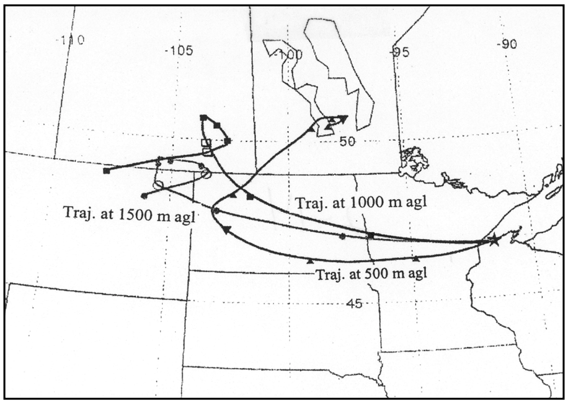


Figure 2-15. HYSPLIT 48 hr back trajectory for Trout Lake MDN at 1 PM CDT, April 17, 2002

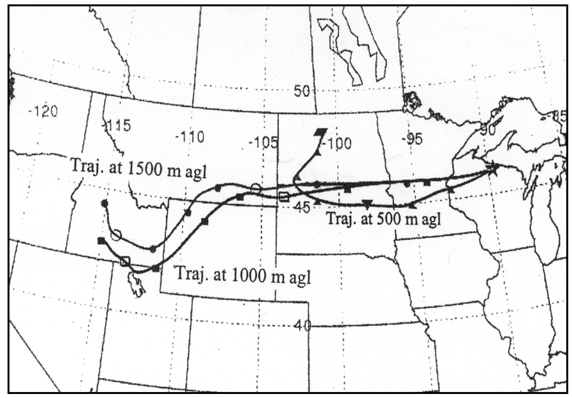


Figure 2-16. HYSPLIT 48 hr back trajectory for Popple River MDN at 1 PM CDT, April 17, 2002

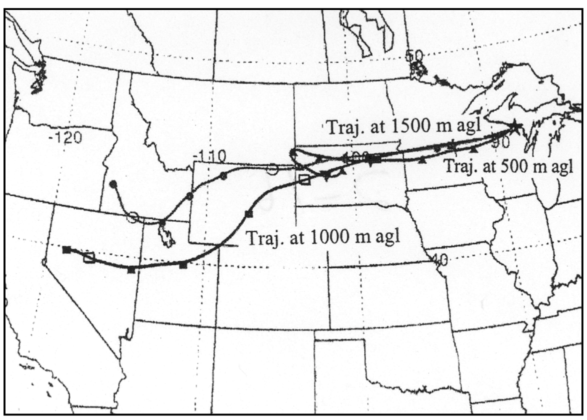


Figure 2-17. HYSPLIT 48 hr back trajectory for Middle Village MDN at 1 PM CDT, April 17, 2002

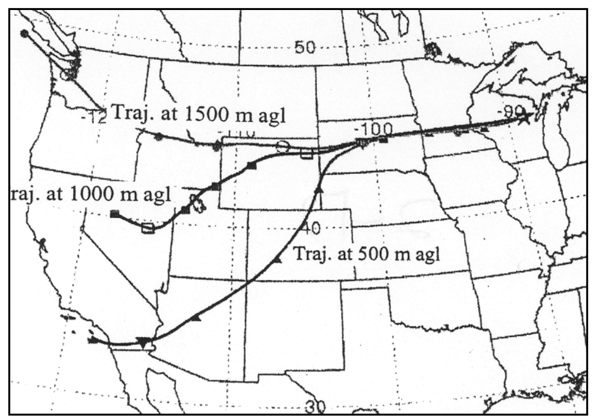


Figure 2-18. HYSPLIT 48 hr back trajectory for Devil's Lake MDN at 1 PM CDT, April 17, 2002

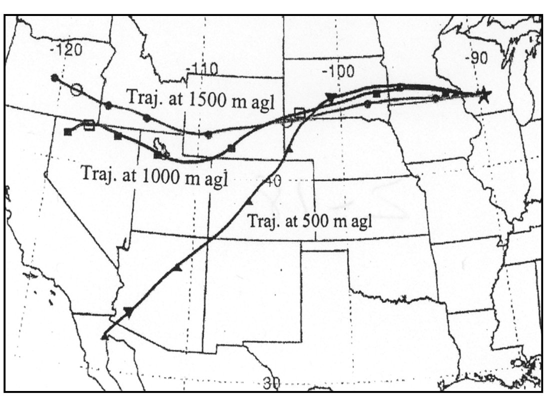


Figure 2-19. HYSPLIT 48 hr back trajectory for L. Geneva MDN at 1 PM CDT, April 17, 2002

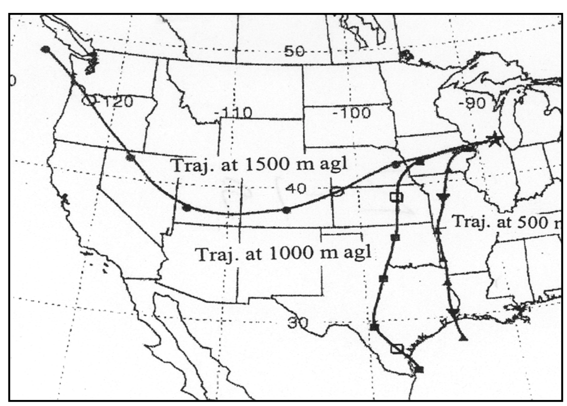


Figure 2-20. HYSPLIT 48 hr back trajectory for Brule River MDN at 1 PM CDT, April 18, 2002

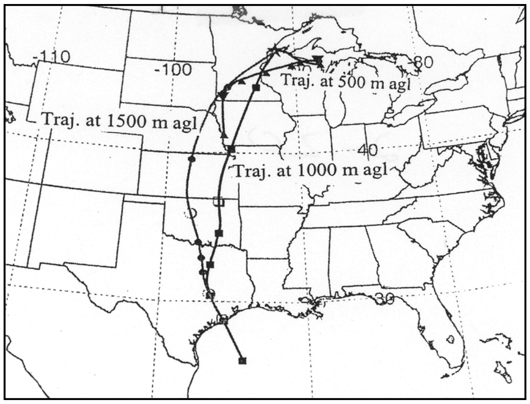


Figure 2-21. HYSPLIT 48 hr back trajectory for Trout Lake MDN at 1 PM CDT, April 18, 2002

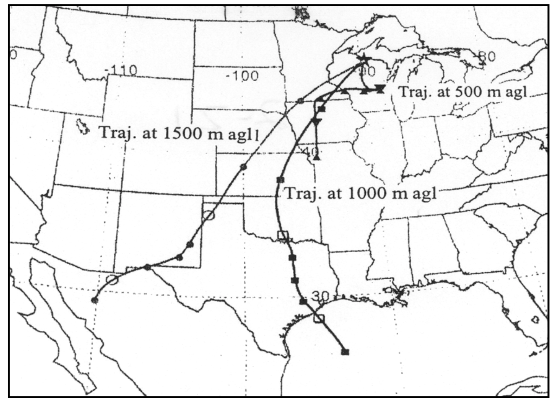


Figure 2-22. HYSPLIT 48 hr back trajectory for Popple River MDN at 1 PM CDT, April 18, 2002

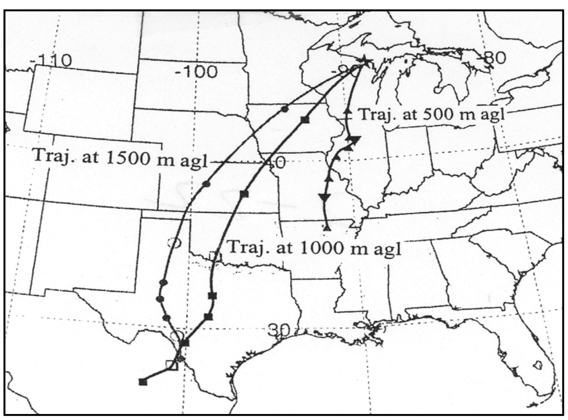


Figure 2-23. HYSPLIT 48 hr back trajectory for Middle Village MDN at 1 PM CDT, April 18, 2002

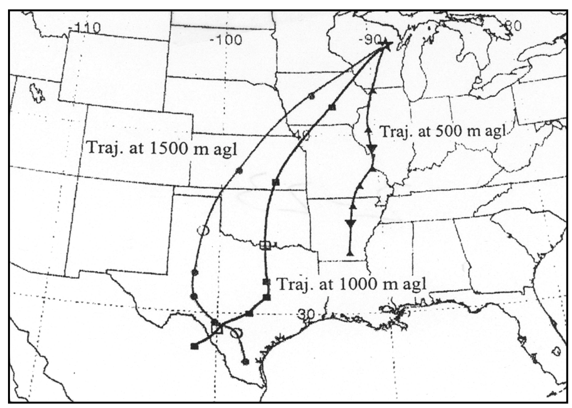


Figure 2-24. HYSPLIT 48 hr back trajectory for Devil's Lake MDN at 1 PM CDT, April 18, 2002

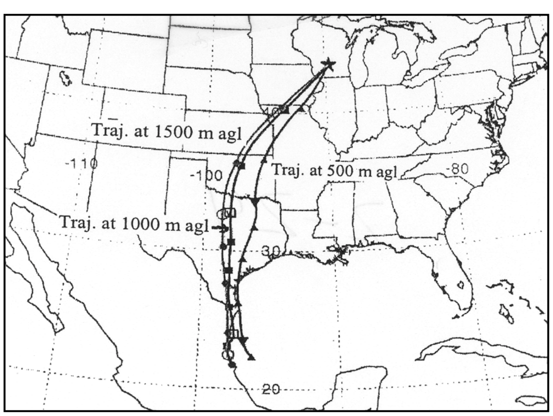
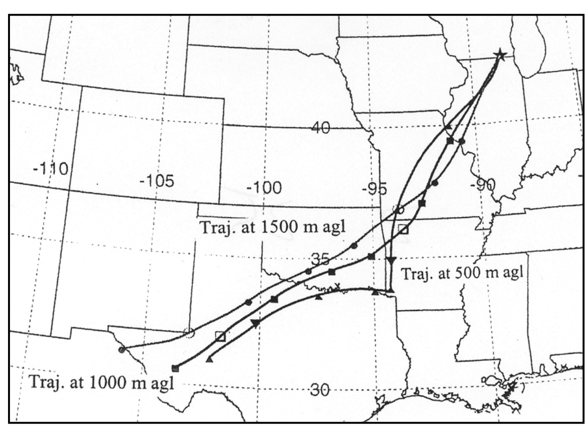


Figure 2-25. HYSPLIT 48 hr back trajectory for Lake Geneva MDN at 1 PM CDT, April 18, 2002



III. Atmospheric Chemistry Model

A) CAMx

CAMx is an Eulerian model that allows for an integrated "one-atmosphere" treatment of particle and gaseous air pollution. It is designed to include all of the technical features needed in a "state-of-the-science" air quality model. The input/output file formats are compatible with many existing pre- and post-processing tools.

CAMx simulates the emission, dispersion, chemistry, and removal of pollutants in the lower troposphere by solving the continuity equation for each pollutant on a three-dimensional grid system. The continuity equation describes the change in pollutant concentration with time, in a given volume of air, as the sum of all physical and chemical processes impacting on that volume.

CAMx can be used with several types of map projections and the vertical grid structure can be defined by the user so layer heights may be specified as any arbitrary function of space and/or time. A complete description of the general CAMx model can be found the CAMx User's Guide, version 4.00 (ENVIRON, 2004).

The CAMx model has been expanded to simulate mercury. This gives CAMx the capability to model the chemical transformations of gaseous elemental mercury, Hg(0), reactive divalent mercury, Hg(II), and particulate mercury, Hg(p) from their emission source to deposition through wet and dry processes. Modifications to CAMx version 4.02 included a new chemistry module to treat the gas- and aqueous-phase chemistry of mercury species. There were also improvements to the dry deposition module to better resolve differences between seasons and the effects of snow cover. All of the details involving the above-mentioned improvements to CAMx can be found in ENVIRON's and AER's final report to the WDNR, "Modeling Atmospheric Mercury Chemistry and Deposition with CAMx for a 2002 Annual Simulation", (Yarwood, Lau, Jia, Karamchandani, & Vijayaraghavan, 2003).

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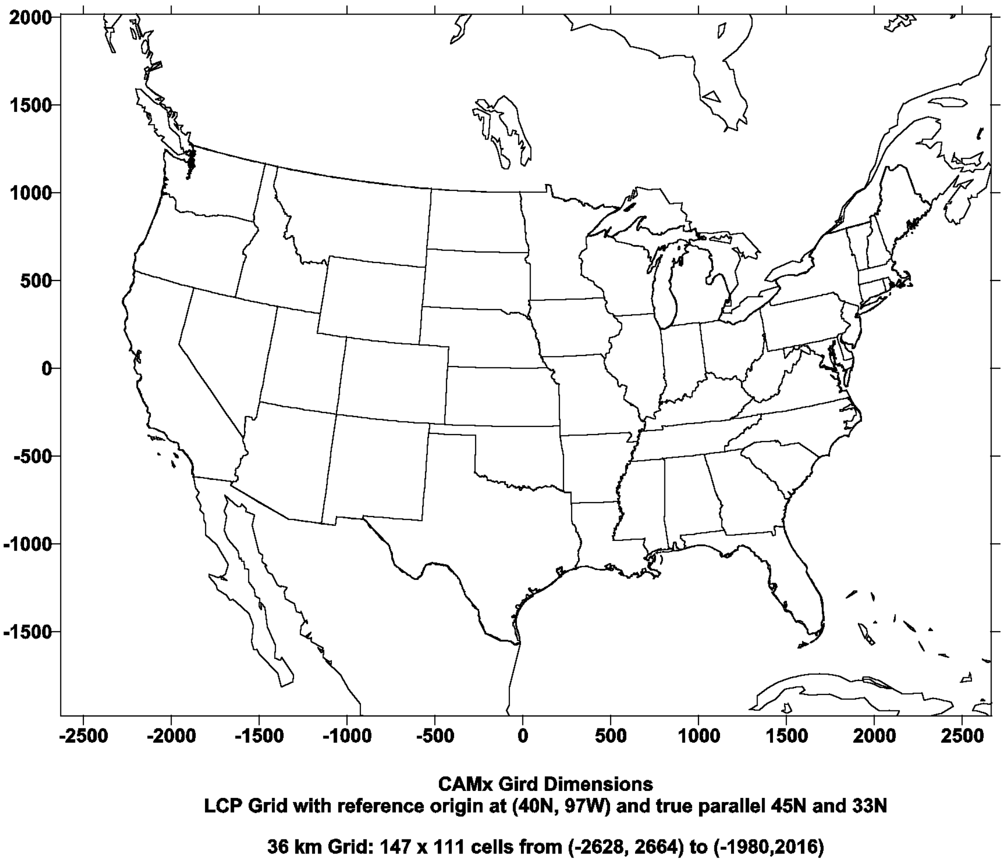
B) Modeling Domain for Episodic Modeling

ENVIRON's evaluation of their 2002 annual run showed that the modeled mercury wet deposition was consistently higher than the observed values by a factor of 2 to 3. One of the main causes for the over-prediction was identified to be an unexpectedly large influence of the top boundary conditions for Hg (II). For ENVIRON's study the model top was set at about 7 km.

The Hg (II) removed from the upper levels of the model was replenished from the boundary conditions by vertical motions through the model top. ENVIRON's recommendation, for mercury modeling, would be to extend the model top above 10 km. In the current modeling, this was accounted for by setting the model top between 11 and 12 km. The details of the model layers and the correspondence between the MM5 and CAMx layers are included in the discussion of meteorological modeling (Table 4-5).

The chemistry modeling domain was the 36 km resolution National Regional Planning Organization (RPO) grid covering the entire continental United States, and parts of Mexico and Canada (Figure. 3-1). The coarse grid domain had 147 by 111 36 km grid cells with a grid origin, in Lambert coordinates, of –2628 km West and –1980 km North.

Figure 3-1. CAMx modeling domain with 36 km grid resolution



Inside of the coarse grid was a 12 km fine grid centered on Wisconsin (Figure 3-2). This grid had 128 grid cells in the x-direction by 110 grid cells in the y-direction. This fine grid was used to give better resolution to the general predicted precipitation pattern and especially areas of deeper convection.

C) Episode Selection

The mercury deposition event selected was the seven day period from April 16 through April 22, 2002. MDN deposition data and site location information is given in Table 3-1. While concentrating on the rainfall deposition event in Wisconsin, twelve different sites across the Midwest were used for prediction/observation comparisons. Locations of the mercury monitoring sites are shown in Figure 3-3 (retrieved April 1, 2004, from http://nadp.sws.uiuc.edu/mdn/sites.asp). Several notes about this episode: the Lake Geneva monitor recorded its highest weekly deposition of the year during this period, 1100.4 ng/m2. The Popple River site also recorded its highest deposition of the year during this period, 1164.2

Figure 3-2. The CAMx fine grid domain with 12 km resolution

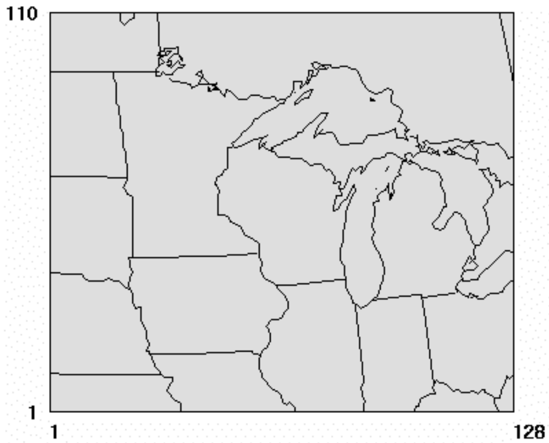
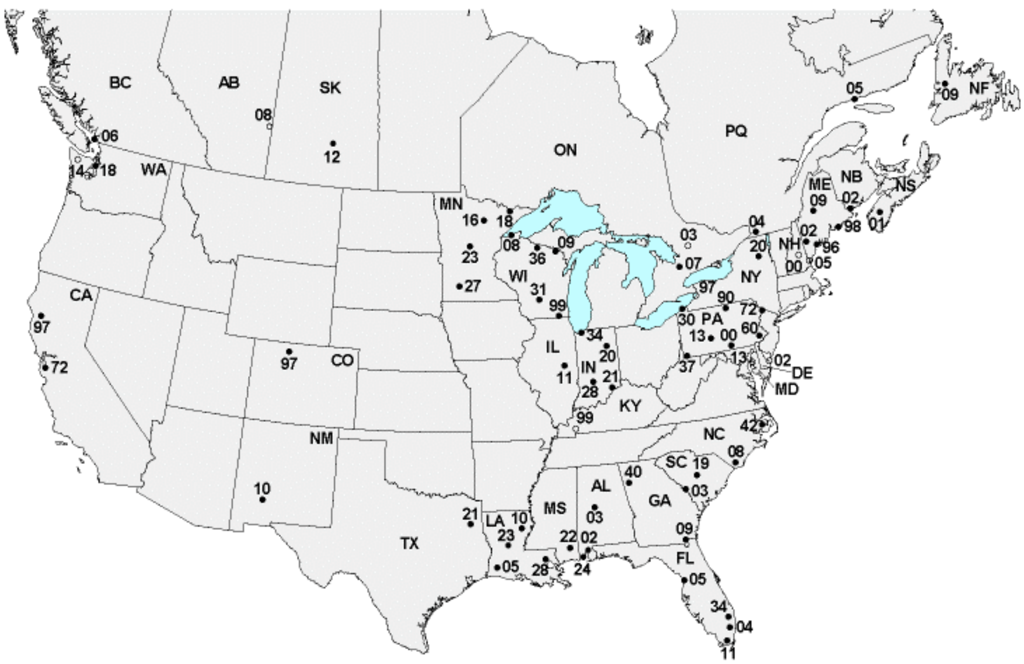


Figure 3-3. Mercury Deposition Network monitoring sites



ng/m2. Trout Lake recorded 895.4 ng/m2, Brule River recorded 418.7 ng/m2, both mid-range values. The Devil's Lake monitoring site, which has a different monitoring time period, measured 1124.0 ng/m2 during the period of April 15-22. This is the second highest multi-day event at Devil's Lake. Thus, there appears to be a good north-south continuity in the deposition coverage over a large area. All sites received deposition during the period.

A review of archived precipitation data measured at 14 National Weather Service (NWS) sites during this period indicate that most of the rainfall took place during April 17th to 19th .

Table 3-1. Midwest MDN site deposition for the period of April 16 through April 22, 2002

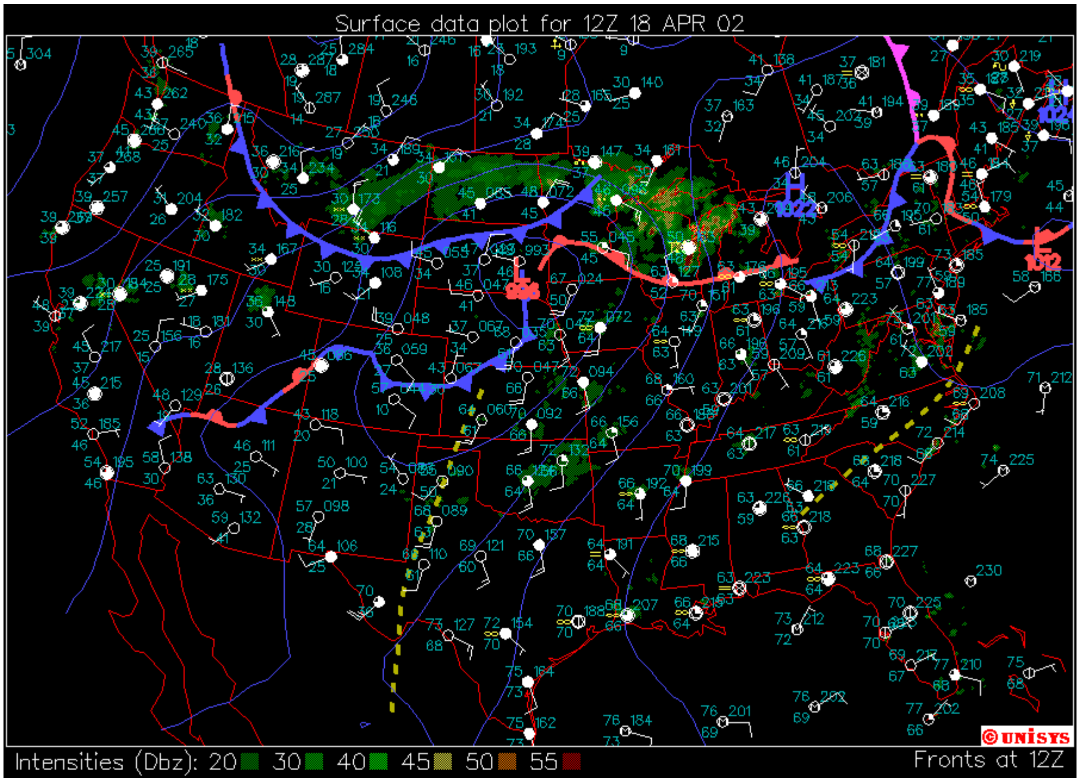
Station Name	Station ID	Latitude	Longitude	County	Hg Deposition (ng/m^2)
Wisconsin					
Brule River	WI08	46.74	-91.60	Douglas	418
Trout Lake	WI36	46.05	-89.65	Vilas	895
Popple River	WI09	45.79	-88.39	Florence	1164
Devil's Lake	WI31	43.43	-89.68	Sauk	1124
Lake Geneva	WI99	42.57	-88.50	Walworth	1100
Minnesota					
Lamberton	MN27	44.23	-95.30	Redwood	277
Fernberg	MN18	47.94	-91.49	Lake	125
Camp Ripley	MN23	46.24	-94.49	Morrison	591
Indiana					
Indiana Dunes	IN34	41.63	-87.08	Porter	899
Roush Lake	IN20	40.84	-85.46	Huntington	263
Clifty Falls	IN21	38.76	-85.42	Jefferson	867
Illinois					
Bondville	IL11	40.05	-88.37	Champaign	273

The weather pattern over this seven day period included the passage of several weather fronts across Wisconsin. However, most of the wet deposition would have occurred with an event centered around the 18th and 19th of the month. The surface data plot for 12Z 18 April is shown in Figure 3-4. A low pressure center at the surface and the 850 mb level was located over eastern South Dakota. The circulation around this feature was bringing warmer and moister air northward and lifting it up over a warm front across southern Wisconsin. The result of this lift was an area of rain showers and thundershowers over the northeast half of Wisconsin and the Upper Peninsula of Michigan. Just to the northwest of the low center was a cold front moving southward into the northern Plains.

By 00Z 19 April (Figure 3-5) the surface low pressure center had moved into western Wisconsin with a warm front extending to the northeast of the low. A cold front stretched southwest of the low through western Iowa into central Kansas. Showers and thunderstorms were occurring ahead of the cold front from Wisconsin to Kansas. Radar echoes indicate showers occurring over much of Wisconsin both in the warm sector and to the north of the warm front.

On 19 April 12Z (Figure 3-6) the surface low center had raced into southeastern Canada and the cold front has reached parts of southern Indiana and Illinois. All of the showers had moved south as high pressure began to build into Wisconsin.

Figure 3-4. Surface plot and radar echoes for 12Z April 18, 2002



D) Boundary Conditions

The development of the boundary values is described in the ENVIRON report to the WDNR (Yarwood, 2003). Mercury boundary conditions were derived from concentrations simulated over North America by a global transport model. There was mapping between each CAMx boundary grid cell and the nearest global boundary cell. Also, there was vertical mapping between the 17 CAMx layers and the global model's nine layers. The global model extended to the lower stratosphere. The mercury boundary conditions were developed for the four seasons and values for the "spring" season were used for this episode.

Figure 3-5. Surface plot and radar echos for 00Z April 19, 2002

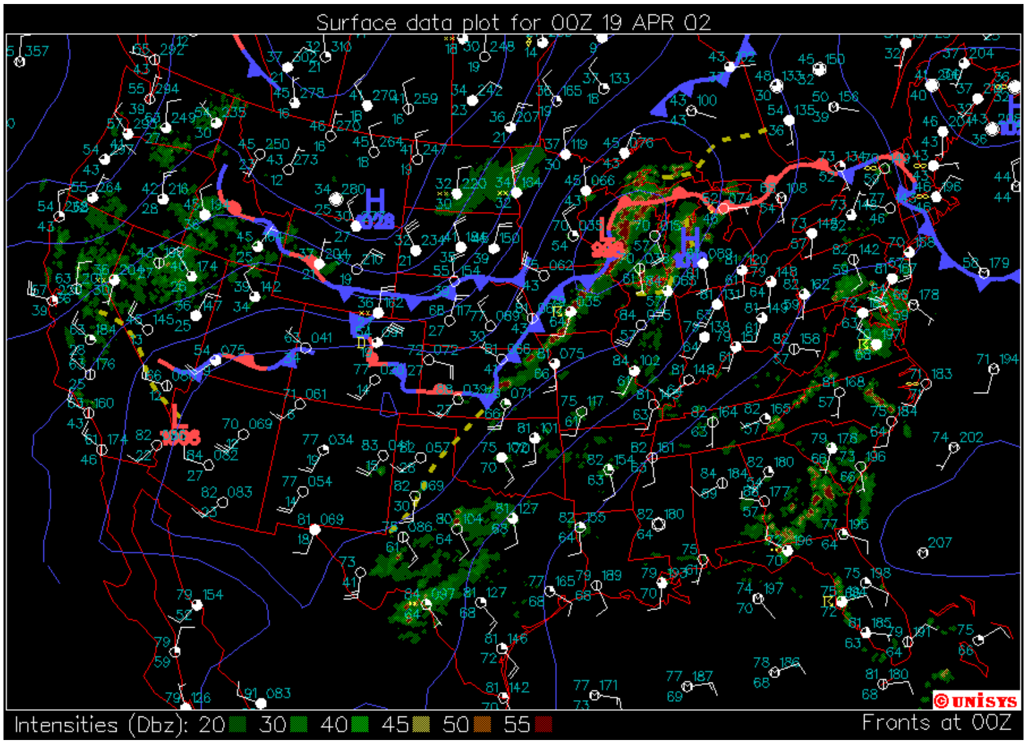
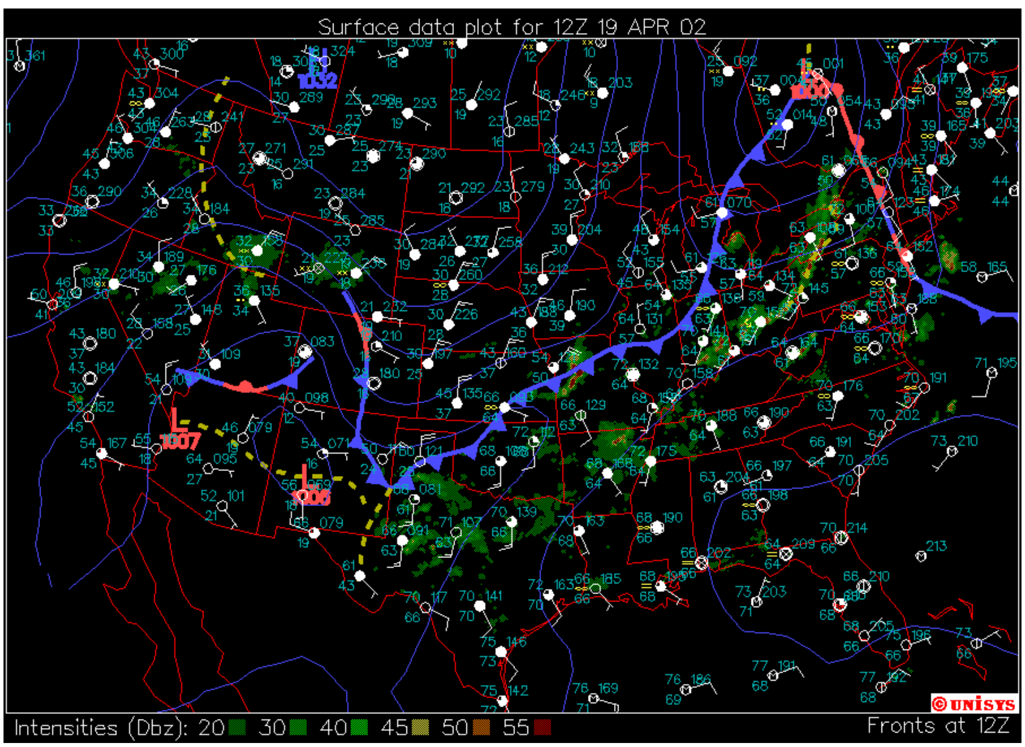


Figure 3-6. Surface plot and radar echos for 12Z April 19, 2002



IV. Meteorological Model

A) Background

The overall objective of the meteorological modeling for this project was to develop a realistic meteorological field for assessment of mercury transport and deposition over the Midwest. Regional mercury models require accurate information on the temperature, humidity levels, diffusivity, cloud cover, precipitation, wind speed and direction to determine mercury circulation and distribution under various weather situations. Consequently, the meteorology fields used to drive the mercury model play a crucial role in understanding mercury deposition in the atmosphere. In order to address the above-mentioned objective well, two mercury episodes were selected for our meteorological modeling: a) 2002 annual episode, and b) April 2002 episode.

The 2002 annual episode provides us the most recently available mercury and meteorology observations, weather reports and emissions database. Regarding the meteorology conditions for the year 2002, the National Climatic Data Center (National Climatic Data Center, 2002) reported that it was warmer than average for the U.S. with a temperature of 53.9F which was 1.1F above the long-term average. The year began with above average warmth, especially in the Northeast, and gradually ended with cooler than normal to near average temperatures across much of the nation. Precipitation was characterized by dryness in the west, above average wetness in the Mississippi Valley Region and dryness changing to near average for the east. Overall, it was a typical weather scenario for Midwest.

During the second half of April, 2002, most parts of Wisconsin experienced both extremely high mercury and precipitation as reported by the National Atmospheric Deposition Program-Mercury Deposition Network (MDN) and National Weather Service. These conditions provide ideal mercury and meteorology circumstances to investigate the wet and dry mercury deposition over the region and reconcile differences between mercury deposition predicted by the model and field studies. It also allows us to understand mercury transport and deposition relevant to the heavy rainfalls over Midwest. Consequently, the April 2002 episode was chosen with the meteorology modeling beginning April 11th and ending on April 24th , a total of 13 days.

B) Annual MM5 Model Configuration

The meteorological fields used to drive the photochemical model were produced by the Penn State/NCAR Mesoscale model MM5 version 3.5. The model configuration for the annual simulation is almost the same as many other MM5 configurations, including the annual MM5 modeling performed by Alpine Geophysics for EPA (McNally & Tesche, 2002, 2003). The meteorological inputs needed for the CAMx model are listed in Table 4-1. In particular, our annul MM5 simulation run started on Jan. 1, 2002 and ended on Dec. 31, 2002 with a domain that is the same as the LADCO/Midwest Regional Planning Organization (RPO) 36 km grid. The domain had 129x142 grid points and covered the most of the North America, as showed by the coarse grid of Figure 4-1. Atmosphere input data included the NCEP GDAS analysis, NCEP ETA model output, and NCEP surface and upper air data. The model had 34 vertical layers, as listed in Table 4-2. The model also had the simple ice for the moisture scheme, Kain-Fritcsh for cumulus parameterization, Pleim-Xu for PBL and soil model. The four dimensional data assimilation (FDDA) was only invoked above the planetary boundary layer. Model initialization data came from the National Centers for Environmental Prediction (NCEP) ETA model output including the National Center for Atmospheric Research (NCAR) conventional surface and upper air data.

Table 4-1. Meteorological inputs required for CAMx

CAMx Input Parameter	Description
Layer interface height (m)	3-D gridded time-varying layer heights for the start and end of each hour
Winds (m/s)	3-D gridded wind vectors (u,v) for the start and end of each hour
Temperature (K)	3-D gridded temperature and 2-D gridded surface temperature for the start and end of each hour
Pressure (mb)	3-D gridded pressure for the start and end of each hour
Vertical Diffusivity (m^2/s)	3-D gridded vertical exchange coefficients for each hour
Water Vapor (ppm)	3-D gridded water vapor mixing ratio for each hour
Cloud Water (g/m^3)	3-D gridded cloud water content for each hour
Precipitation Water (g/m^3)	3-D gridded precipitation content for each hour

Figure 4-1. MM5 modeling domains for the RPO national 36 km grid (D01) and the inner 12 km grid (D02)

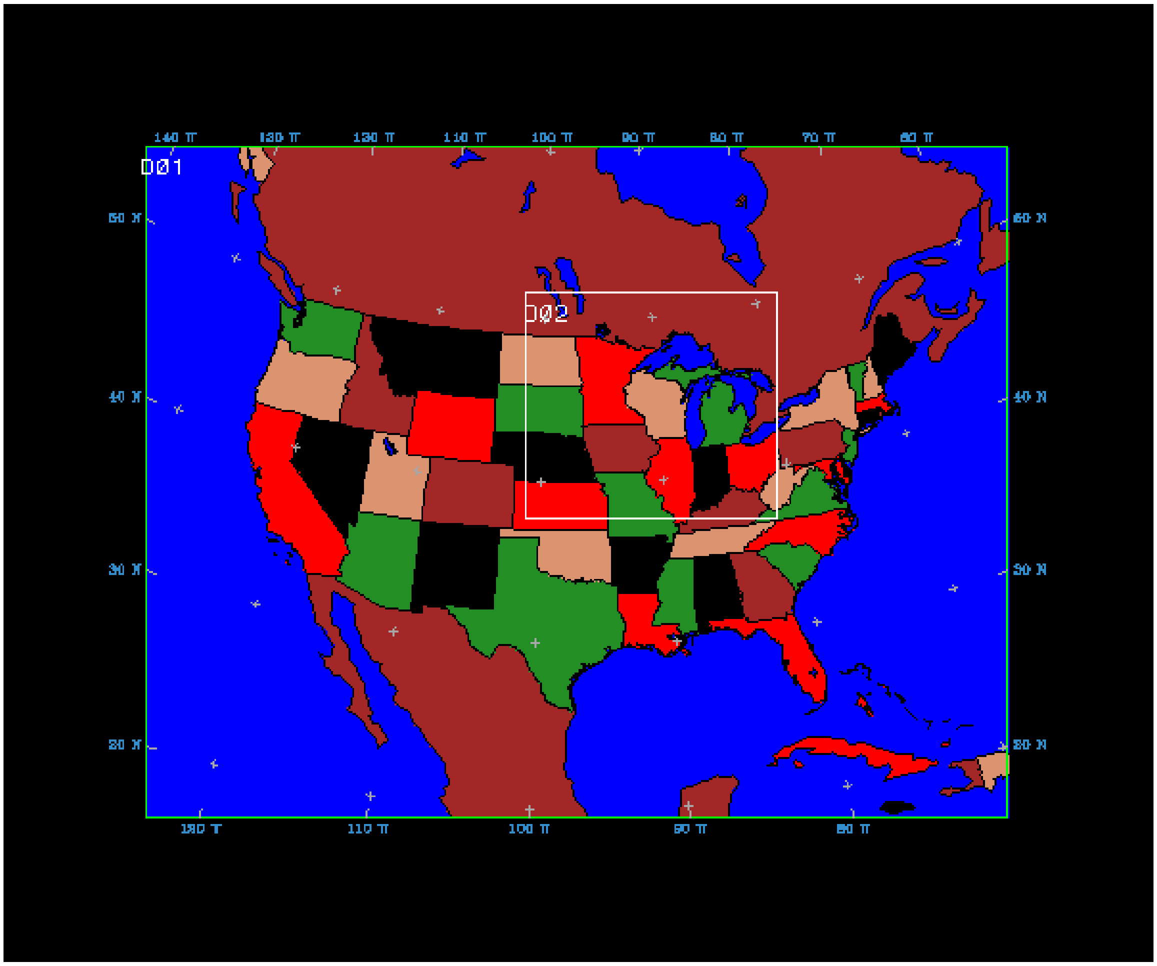


Table 4-2. MM5 vertical grid structures based on 34 sigma-p levels

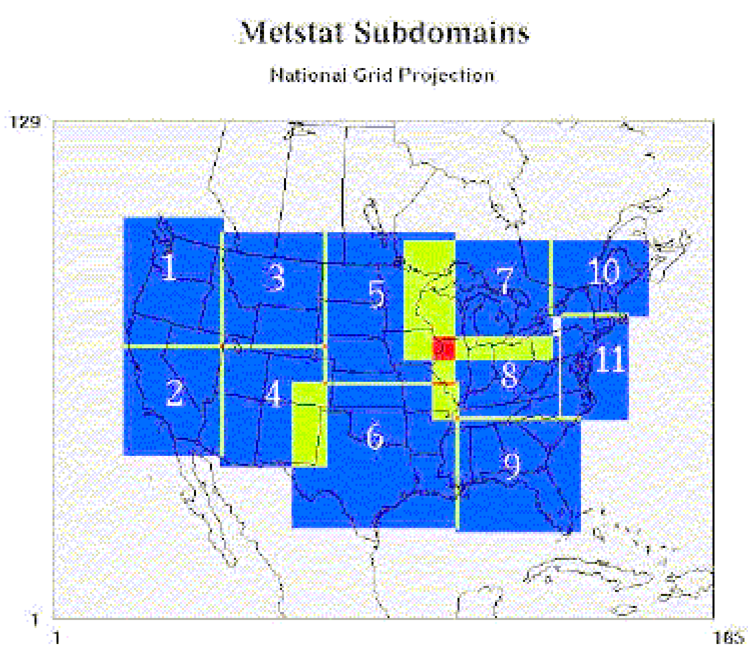
CAMx Layer	MM5 Layer	Sigma Layer	Pressure (mb)	Depth (m)	Height (m)
	34	0.000	100	1841	14661
	33	0.050	145	1466	12820
	32	0.100	190	1228	11354
	31	0.150	235	1062	10126
	30	0.200	280	939	9064
	29	0.250	325	843	8125
14	28	0.300	370	767	7282
	27	0.350	415	704	6515
	26	0.400	460	652	5811
	25	0.450	505	607	5159
13	24	0.500	550	569	4552
	23	0.550	595	536	3983
	22	0.600	640	506	3447
12	21	0.650	685	480	2941
11	20	0.700	730	367	2461
	19	0.740	766	266	2094
10	18	0.770	793	259	1828
	17	0.800	820	169	1569
9	16	0.820	838	166	1400
	15	0.840	856	163	1234
8	14	0.860	874	160	1071
	13	0.880	892	158	911
7	12	0.900	910	78	753
	11	0.910	919	77	675
	10	0.920	928	77	598
6	9	0.930	937	76	521
	8	0.940	946	76	445
	7	0.950	955	75	369
5	6	0.960	964	74	294
	5	0.970	973	74	220
4	4	0.980	982	37	146
3	3	0.985	987	37	109
2	2	0.990	991	36	72
1	1	0.995	996	36	36
Surface	0	1.000	1000	0	Surface

C) Annual MM5 Performance Evaluation

Alpine Geophysics (Tesche, McNally, Loomis, Stella, & Wilkinson, 2004) performed a comprehensive model performance evaluation for our 2002 annual episode for the temperature, wind, and annual rainfall. After comparing over 50 historical runs, they state that the meteorological fields from our 2002 annual episode are acceptable to be used as the input files for the mercury deposition model. Wisconsin Department of Natural Resources (WDNR) completed a similar model performance evaluation and some inconsistencies between the model runs surfaced later in regard to the temperature and annual rainfall fields. Our temperature bias and gross error were analyzed using METSTAT, a widely used software package designed to examine the MM5 model output and capable of comparing and displaying the differences between the MM5 estimates and observation. Alpine Geophysics used MAPS, a public domain software package used to support performance evaluation with MM5. Both parties evaluated the temperature fields by using the same MM5 estimates (the first layer of MM5 output) and observation (NCAR ds472.0).

For analysis, the continental U.S. is divided into eleven sub-regions as displayed by Figure 4-2. The analyzed results for each sub-region for two-month windows are presented in Tables 4-3 and 4-4, respectively. The tables indicate that the temperature bias is comparable to what the contractor had within their report. For the full year within the eleven sub-regions, the bias in hourly surface temperature is –0.96 K for the WDNR analysis and –0.45K for the contractor analysis. WDNR's bias was about 0.41K lower than the contractor's which is in an acceptable error range. Ironically, the difference in the gross error is a little bigger. WDNR's mean gross error for the full year is 2.20K while the contractor's is 3.63K (about 1.43K higher). WDNR's result is very close to many other MM5 annual simulations. WDNR has not performed the analysis to explain the reason behind this, and an investigation is needed in the future.

Figure 4-2. The eleven sub-regions over continental US



Courtesy of Matthew Johnson, IDNR

Table 4-3. Temperature bias (K) for each sub-region and time period for 2002 annual episode

Region	Jan-Feb	Mar-Apr	May-Jun	Jul-Aug	Sep-Oct	Nov-Dec	Mean
ALL	-1.66	-1.49	-0.63	-0.37	-0.26	-1.36	-0.96
1	-2.58	-2.81	-1.65	-0.65	-0.69	-1.75	-1.69
2	-0.6	-0.63	-0.75	-0.76	-0.7	-0.63	-0.68
3	-2.11	-2.73	-2.12	-0.65	-1.31	-2.88	-1.97
4	-2.22	-2.02	-1.64	-1.58	-0.94	-2.03	-1.74
5	-1.88	-1.55	-0.04	0.25	-0.12	-1.83	-0.86
6	-1.12	-0.54	-0.25	-0.51	0.14	-0.5	-0.46
7	-1.97	-1.72	0.05	0.23	0.05	-1.79	-0.86
8	-2.27	-1.34	0.06	-0.04	0.37	-1.38	-0.77
9	-0.31	-0.4	-0.22	-0.3	-0.18	0.44	-0.16
10	-1.78	-2.18	-0.27	0.28	0.08	-1.93	-0.97
11	-1.37	-0.49	-0.12	-0.34	0.4	-0.7	-0.44

Table 4-4. Temperature error (K) for each sub-region and time period for 2002 annual episode

Region	Jan-Feb	Mar-Apr	May-Jun	Jul-Aug	Sep-Oct	Nov-Dec	Mean
ALL	2.53	2.65	2.13	1.87	1.72	2.27	2.20
1	2.93	3.44	2.95	2.4	2.13	2.45	2.72
2	2.12	2.18	2.18	2.32	2.14	1.85	2.13
3	3.15	3.74	3.29	2.2	2.39	3.36	3.02
4	3.13	3.38	3.16	2.99	2.36	2.9	2.99
5	2.47	2.65	1.87	1.44	1.55	2.29	2.05
6	2.18	2.0	1.59	1.6	1.36	1.74	1.75
7	2.44	2.69	1.81	1.45	1.45	2.24	2.01
8	2.81	2.55	1.6	1.46	1.32	2.09	1.97
9	1.69	1.63	1.46	1.39	1.26	1.55	1.5
10	2.59	3.01	1.94	1.72	1.66	2.55	2.25
11	2.34	1.91	1.58	1.65	1.32	1.9	1.78

The contractor also performed an evaluation with the 2002 annual rainfall fields. They pointed out that the WDNR 2002 annual episode overestimates the annual rainfall by 6.35 cm. WDNR calculated the annual rainfall produced by our 2002 episode and compared it with the observation as well, and the results are displayed by Figures 4-3, 4-4 and 4-5. The observed annual rainfall map, Figure 4-3, is based on the NCEP 0.25-degree US daily precipitation analysis and does not include any rainfall outside the continental US. The map shows that annual rainfall of less than 30 cm was experienced over the Dessert Southwest, with about 90 cm over the South Central Region and more than 150 cm over Southeast Region. Most parts of the western half of US experienced annual rainfall between 30 and 150 cm. The eastern half of the US experienced between 100 and 150 cm. The MM5 results show a similar annual rainfall pattern for the continental US, as illustrated by Figure 4-4 for the western half and Figure 4-5 for the eastern half. The highs and lows generally match the observations. However, the figures also show that MM5 overestimates the rainfall by at lest 30 cm overall for the continental US. The

MM5 estimates were about 60 cm for the Southwest, 120 cm for the South Central Region and 180 cm for the Southeast Region. Over the western half of the US, the observations on the whole show that the annual rainfall gradually decreases from the Pacific Northwest moving south and east with rainfall contour lines decreasing from 120 to 30 cm. MM5 also displays a similar rainfall pattern with contour lines decreasing from 150 cm to 60 cm. Over the eastern half of the US, the observation overall shows that the rainfall gradually decreases from south to north and from east to west, with contour lines decreasing from 150 cm to 90 cm. MM5 shows the same rainfall pattern with contour lines decreasing from 220 cm to 90 cm. The previous three rainfall figures illustrate that the MM5 rainfall prediction is most accurate for the Midwest with about a 10% overestimate. The worst performance is over the Southwest with an overestimate of approximately 100%. The model overall overestimates the annual rainfall between 40% and 70%, and on average overestimates the annual rainfall by at least 30 cm for the continental US. This is much higher than the 6.35 cm reported by the contractor for the entire 36 km domain. Since about half of the 36 km grid is over the oceans, as displayed by Figure 4-1, with only a few observations available in a few limited areas, their conclusions may be questionable for those regions over the oceans.

Figure 4-3. The observed annual rainfall for the year 2002 for the continental US

The unit is in cm, and the contour line interval is 30 cm.

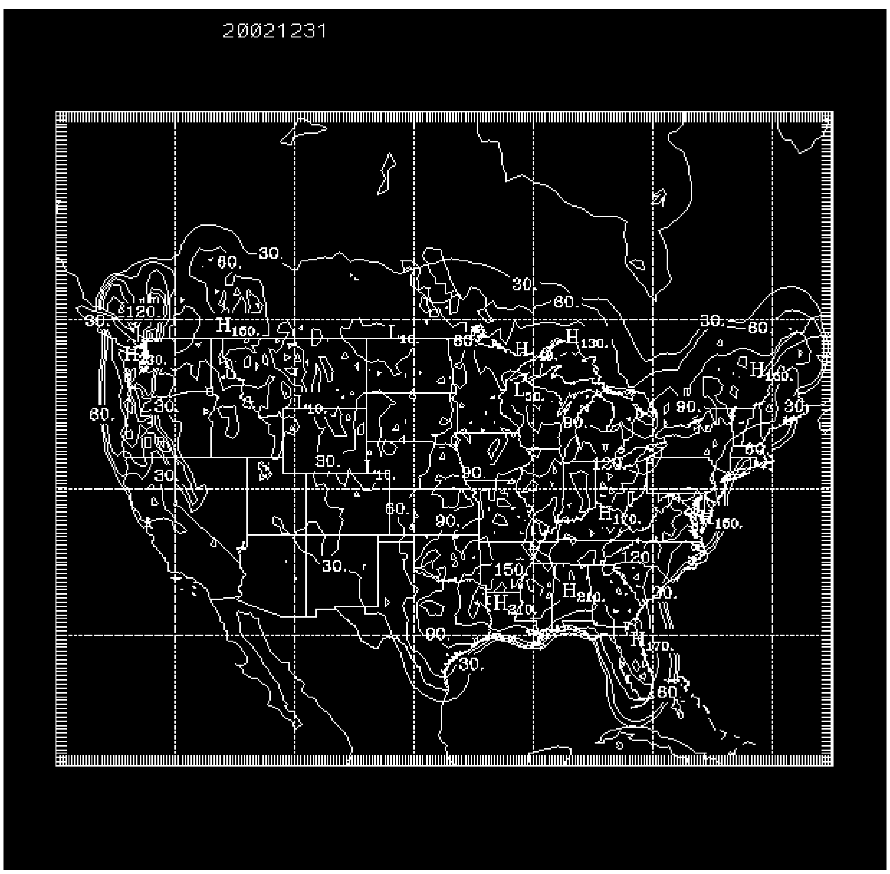


Figure 4-4. MM5 predicted annual rainfall for the year 2002 for the western half of the North America

The unit is in cm, and the contour line interval is 30 cm.

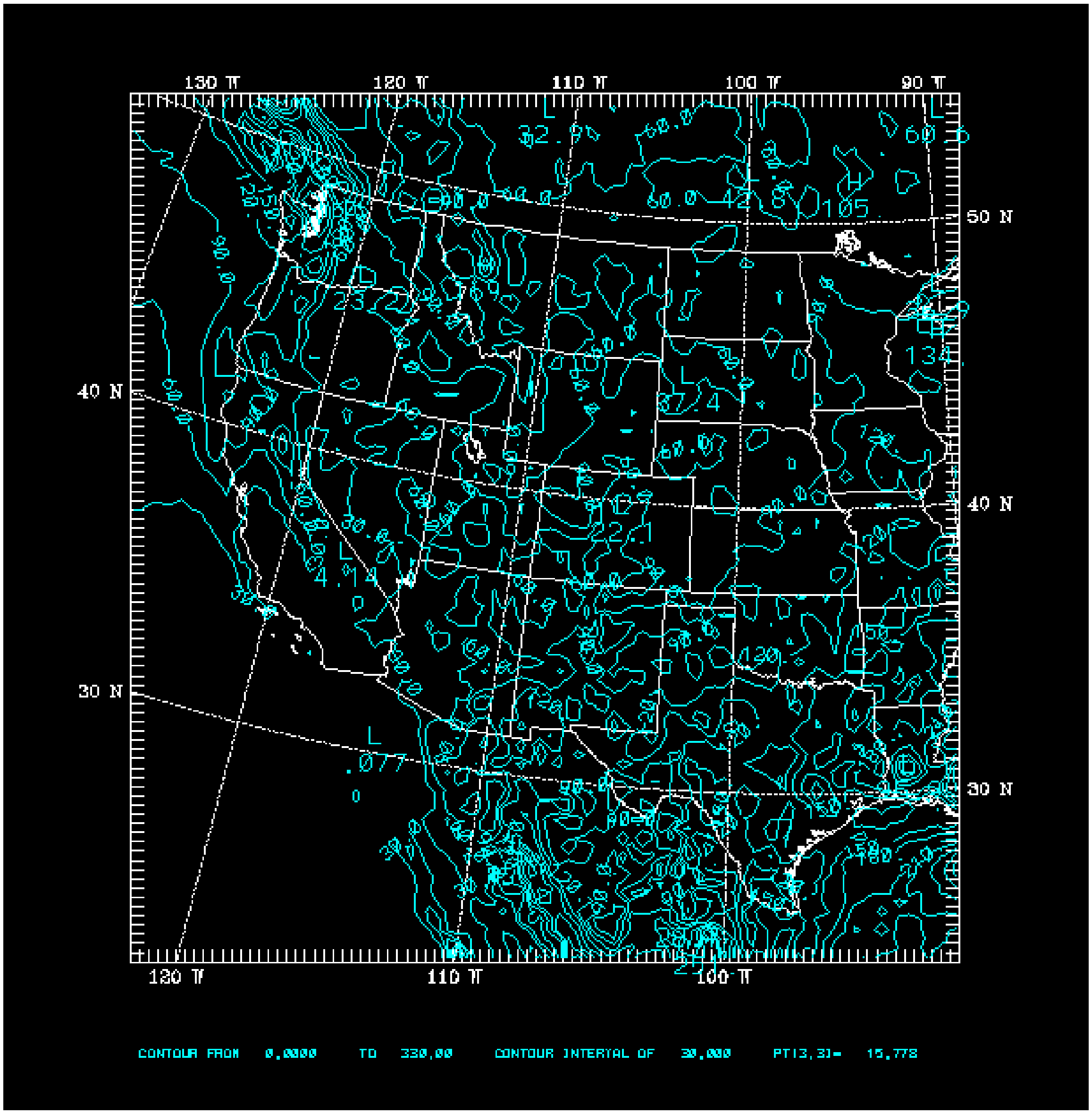
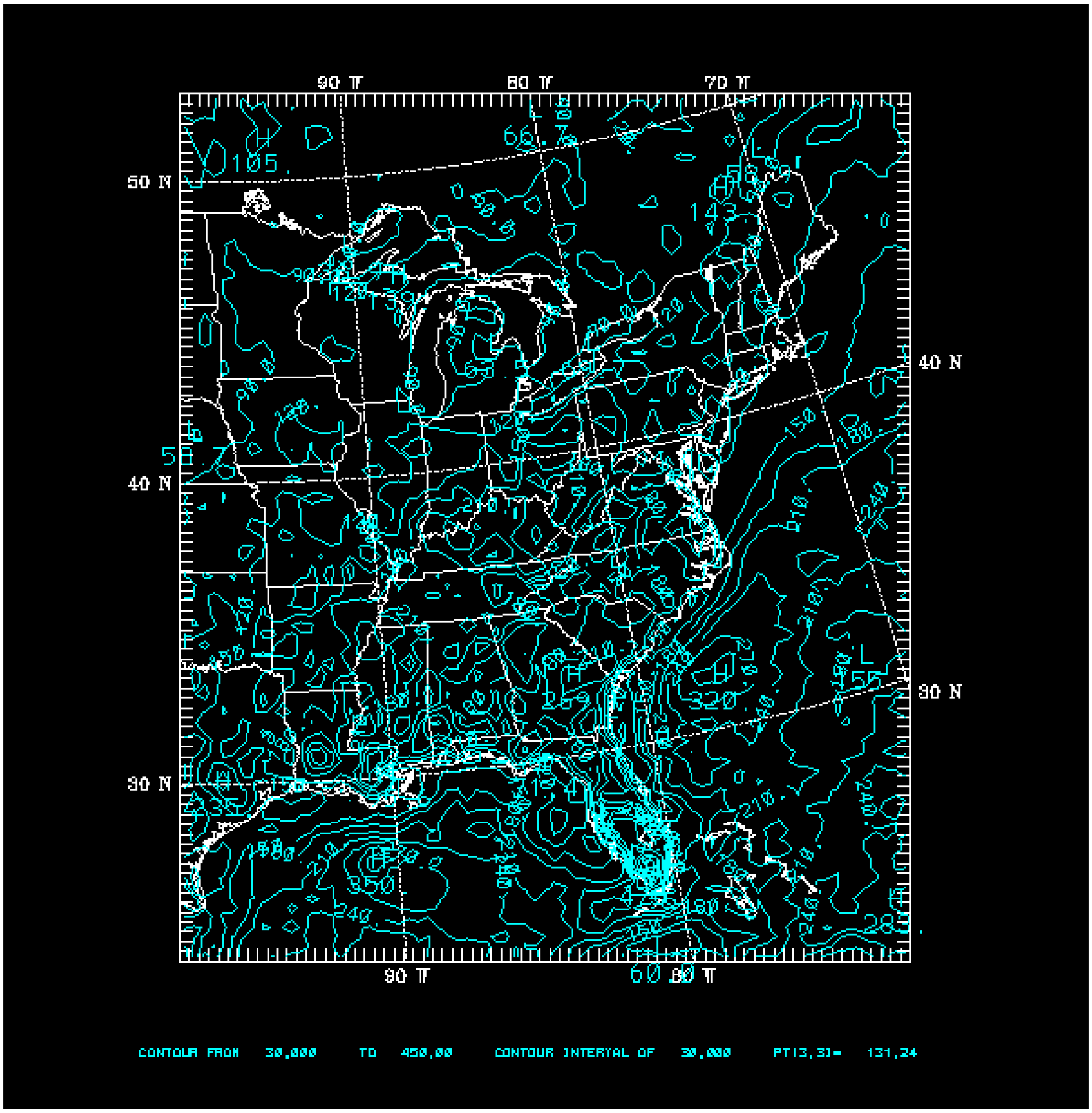


Figure 4-5. MM5 predicted annual rainfall for the year 2002 for the eastern half of the North America

The unit is in cm, and the contour line interval is 30 cm.



D) Episode Model Configuration

Considering the rainfall shortfall with the annual MM5 simulation, a few changes were made with the model configuration for the April 2002 episode with an effort to improve the rainfall estimate. The April 2002 episode uses the same MM5 settings as the 2002 annual episode except the cloud microphysics and the structure of the horizontal and vertical grids. Specifically, a 12 km fine grid centered over Wisconsin with 165x145 grid cells is embedded within the coarse 36 km RPO grid (Figure 4-1). Model simulation started at 1200 UTC April 11, 2002, and ran through 1200 UTC April 24, 2002. This allows for several days of ramp-up before the mercury deposition episode begins on April 16, 2002. Due to a dominating synoptic feature of heavy precipitation during the episode, the modeled vertical layers were increased from 34 half-sigma layers to 46 for both the 36 km and 12 km grids. This provides fine grid spacing for rainfall systems to evolve and develop. The vertical spacing has 36 m vertical spacing in the lowest layers and gradually increases to about 2 km near the model top as displayed by Table 4-5. Over 20 layers are distributed throughout the mid-troposphere to capture cloud and rainfall producing mechanisms and to resolve the atmospheric thunderstorms more accurately.

Table 4-5. MM5 vertical grid structures based on 46 sigma-p levels

CAMx Layer	MM5 Layer	Sigma Level	Pressure (mb)	Depth (m)	Height (m)
	46	0.000	100	2194	15736
	45	0.050	145	1673	13541
17	44	0.100	190	1363	11868
	43	0.150	235	1156	10505
	42	0.200	280	1007	9349
16	41	0.250	325	894	8343
	40	0.300	370	651	7449
15	39	0.340	406	456	6798
	38	0.370	433	433	6342
	37	0.400	460	277	5909
	36	0.420	478	268	5632
14	35	0.440	496	260	5365
	34	0.460	514	252	5105
	33	0.480	532	245	4853
	32	0.500	550	238	4608
	31	0.520	568	232	4370
13	30	0.540	586	226	4138
	29	0.560	604	220	3913
	28	0.580	622	215	3692
	27	0.600	640	210	3478
	26	0.620	658	205	3268
12	25	0.640	676	200	3063
	24	0.660	694	196	2863
	23	0.680	712	192	2668
	22	0.700	730	188	2476
	21	0.720	748	184	2288
11	20	0.740	766	180	2105
	19	0.760	784	177	1924
	18	0.780	802	173	1748

CAMx Layer	MM5 Layer	Sigma Level	Pressure (mb)	Depth (m)	Height (m)
10	17	0.800	820	170	1575
	16	0.820	838	167	1405
9	15	0.840	856	164	1238
	14	0.860	874	161	1074
8	13	0.880	892	158	912
	12	0.900	910	78	754
7	11	0.910	919	78	676
	10	0.920	928	77	598
	9	0.930	937	76	521
6	8	0.940	946	76	445
	7	0.950	955	75	369
5	6	0.960	964	74	294
	5	0.970	973	74	220
4	4	0.980	982	37	146
3	3	0.985	986	37	109
2	2	0.990	991	36	73
1	1	0.995	995	36	36
Surface	0	1.000	1000	0	Surface

Since rainfall systems in the atmosphere are closely associated with warm and cold fronts, the rainfall estimates are also closely coupled with the model's ability to correctly interpolate the warm/cold air mass location and the surface wind/temperature fields. Based on several recent rainfall verification studies (Colle, Steenburg, Cox, & Kingsmill, 2001) and our own MM5 simulation runs, it seems the Reisner Graupel explicit moisture scheme with a finer vertical layer structure would produce the most accurate rainfall fields for this study. In addition, MM5 version 3.5 has a total of eight different cumulus parameterization schemes, of which a few are suitable for our model application. After a series of model sensitivity tests and comparisons with the observations, it seems that the Betts-Miller parameterization scheme produces the most reasonable rainfall estimate for this episode. Therefore, it was selected for this application.

E) Episode MM5 Performance Evaluation

By using similar methods as the 2002 annual model performance evaluation, the modeled rainfall is compared with observations and model temperature and wind fields are analyzed using METSTAT. Figures 4-6 through 4-11 provide examples of the comparison between prediction and observation over the heaviest rainfall hours during the episode. The rainfall maps using simple-ice moisture scheme are extracted from our 2002 annual episode over the 36 km grid. The maps using Reisner moisture scheme are extracted from our April 2002 episode over the 12 km grid. The radar mosaics are from the actual National Mosaic Reflectivity image.

Figure 4-6. Modeled hourly precipitation (mm): simple-ice moisture scheme, 36 km grid. April 18, 2002: 2200-2300 UTC

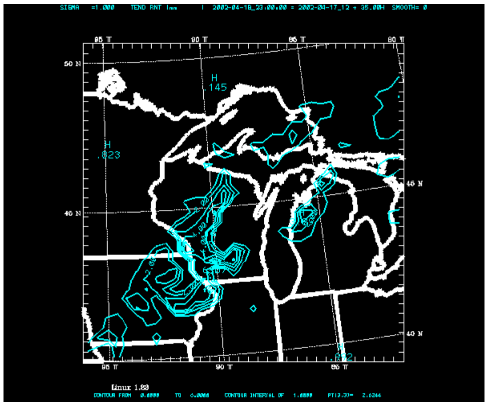


Figure 4-7. Modeled hourly precipitation (mm): Reisner Graupel scheme, 12 km grid. April 18, 2002: 2200-2300 UTC

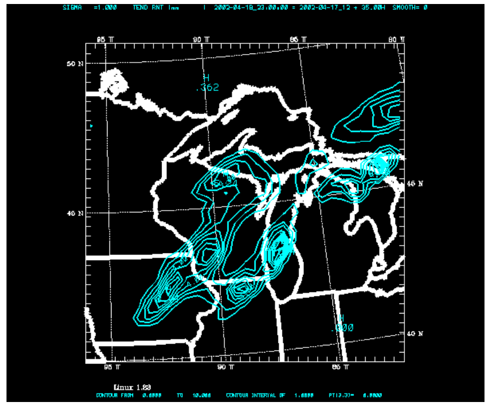


Figure 4-8. Radar mosaic at 2300 UTC: April 18, 2002

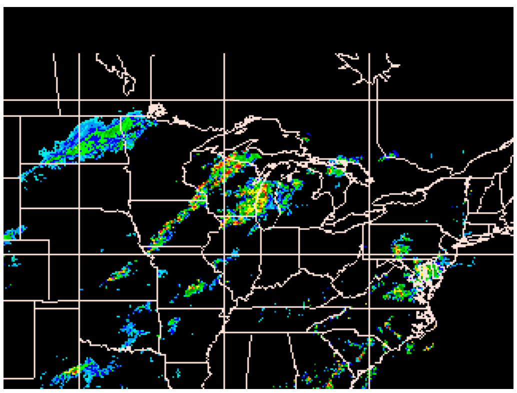


Figure 4-9. Modeled hourly precipitation (mm): simple-ice moisture scheme, 36 km grid. April 19, 2002: 0100-2300 UTC

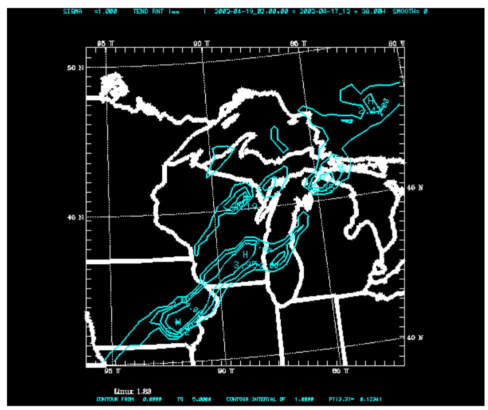


Figure 4-10. Modeled hourly precipitation (mm): Reisner Graupel scheme, 12 km grid. April 19, 2002: 01000-0200 UTC

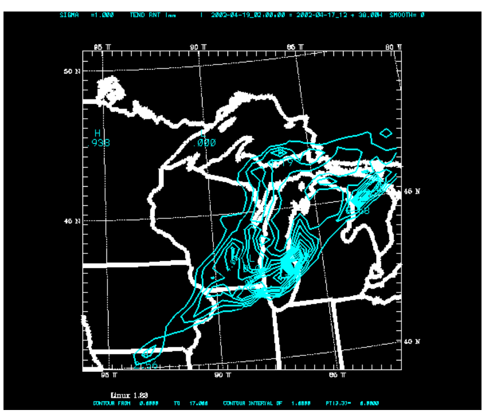
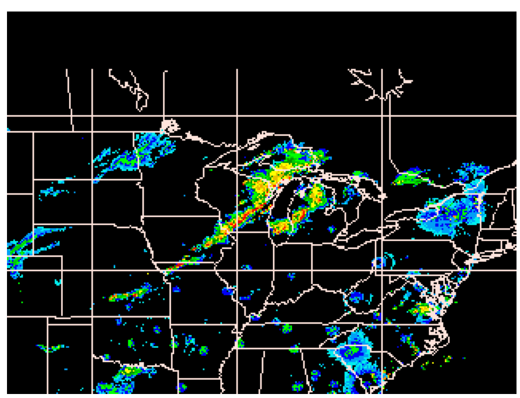


Figure 4-11. Radar mosaic at 0200 UTC: April 19, 2002



The images indicate there is a cold front with intense rainfall stretching from the Upper Peninsula of Michigan through Wisconsin and southwestward to Kansas. There is also a secondary rainfall area parallel to the front over Michigan. At 2300 UTC April 18th (Figures 4-6, 4-7 and 4-8) the simple-ice scheme captures the general location of the front but does not show any precipitation over eastern Wisconsin and Lake Michigan. This scheme also indicates an area of rain over south-central Wisconsin which is missing from the radar mosaic. The Reisner scheme gives a much better match to the radar mosaic. The most obvious improvement is the area of heavier rain predicted from extreme northern Illinois through southeastern Wisconsin and over Lake Michigan. Also, the rain-free area over south-central Wisconsin is better depicted by the Reisner scheme. The cold front precipitation appears in a more linear pattern, similar to that shown on the mosaic. However, the Reisner scheme does not continue the rain along the front southwestward through Iowa. Nor does it predict precipitation in the northwestern part of Lower Michigan as does the simple-ice scheme.

The plots for 0200 UTC April 19th again indicate the Reisner scheme to give a better match to the actual radar pattern (Figures 4-9, 4-10, and 4-11). There are better matches with the precipitation areas over southeastern Lake Superior, Lake Huron, and the area from central Lower Michigan to southern Lake Michigan. The simple-ice scheme has a more linear frontal precipitation band from south-central Wisconsin to southeast Iowa. This is a better match to the radar pattern than the less defined result of the Reisner scheme.

The heaviest 24-hour predicted rainfall within the episode occurs April 19th (Figure 4-12). MM5 with Reisner Graupel scheme is used to predict 24-hour daily rainfall total ending at 1200 UTC of April 19th for Midwest over the 12 km grid. It indicates that a large part of Wisconsin received at least a trace of rainfall and a small portion received at least 48 mm with the maximum of 70 mm over central Wisconsin. A secondary rainfall area was over lower Lake Michigan. The NCEP 0.25-degree observed 24-hour daily rainfall total ends at 1200 UTC April 19th for the Midwest and Wisconsin are shown in Figures. 4-13 and 4-14 respectively. Both figures show that there is a high rainfall area over central Wisconsin with a maximum of 63 mm, about 7 mm less than the Reisner Graupel scheme prediction. The high center was over northern Wisconsin indicating that the Reisner Graupel scheme missed the rainfall center by about 150 km south. Additionally, since there are only a few observation sites available over the lake, the observation maps fail to display the secondary rainfall area over the lake and show only part of it by the highs over both sides of the lake. The secondary rainfall maximum is also verifiable through the hourly radar mosaics (Figures 4-8 and 4-11). These figures demonstrate that the model reasonably predicted the rainfall location and distribution pattern over the lake. The figures also illustrate that the model has a tendency of over predicting rainfall total over land. Looking at the same 24-hour precipitation generated by the simple-ice scheme reveals it also successfully reproduces the rainfall pattern over Wisconsin area with a reasonable rainfall distribution (Figure 4-15). However, the disadvantage is that it underestimates the rainfall total with a maximum of only 32 mm. The simple-ice scheme also has difficulty with the weaker rainfall system and completely misses the precipitation over the lake.

Figure 4-12. MM5 with Reisner Graupel moisture scheme predicted 24-hour daily rainfall total ending at 1200 UTC April 19, 2002 for Midwest in the 12 km grid

The unit is in mm, and the contour line interval is 12 mm.

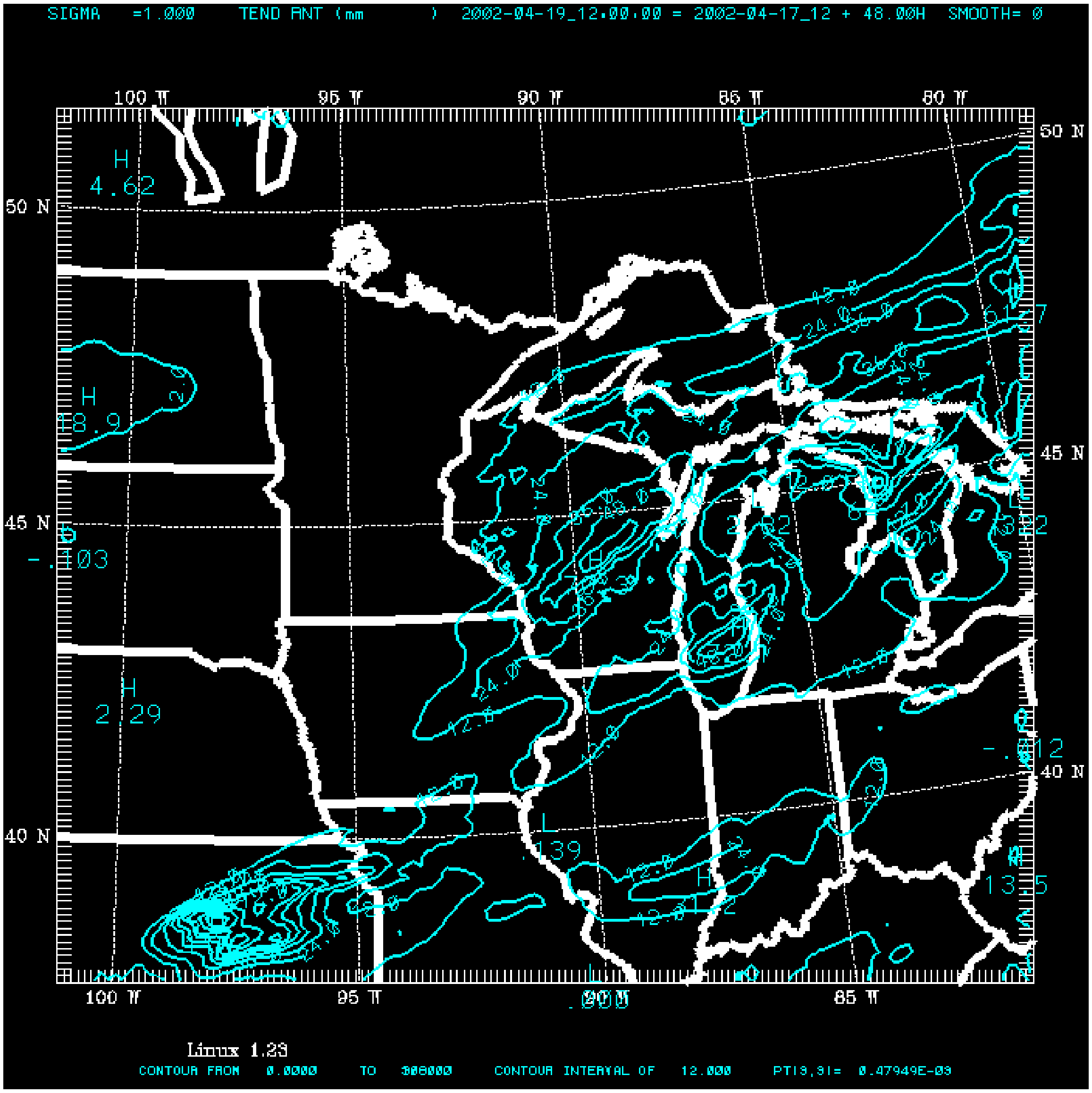


Figure 4-13. NCEP observed 24-hour daily rainfall total ending at 1200 UTC April 19, 2002 for Midwest

The unit is in mm, and the contour line interval is 4 mm.

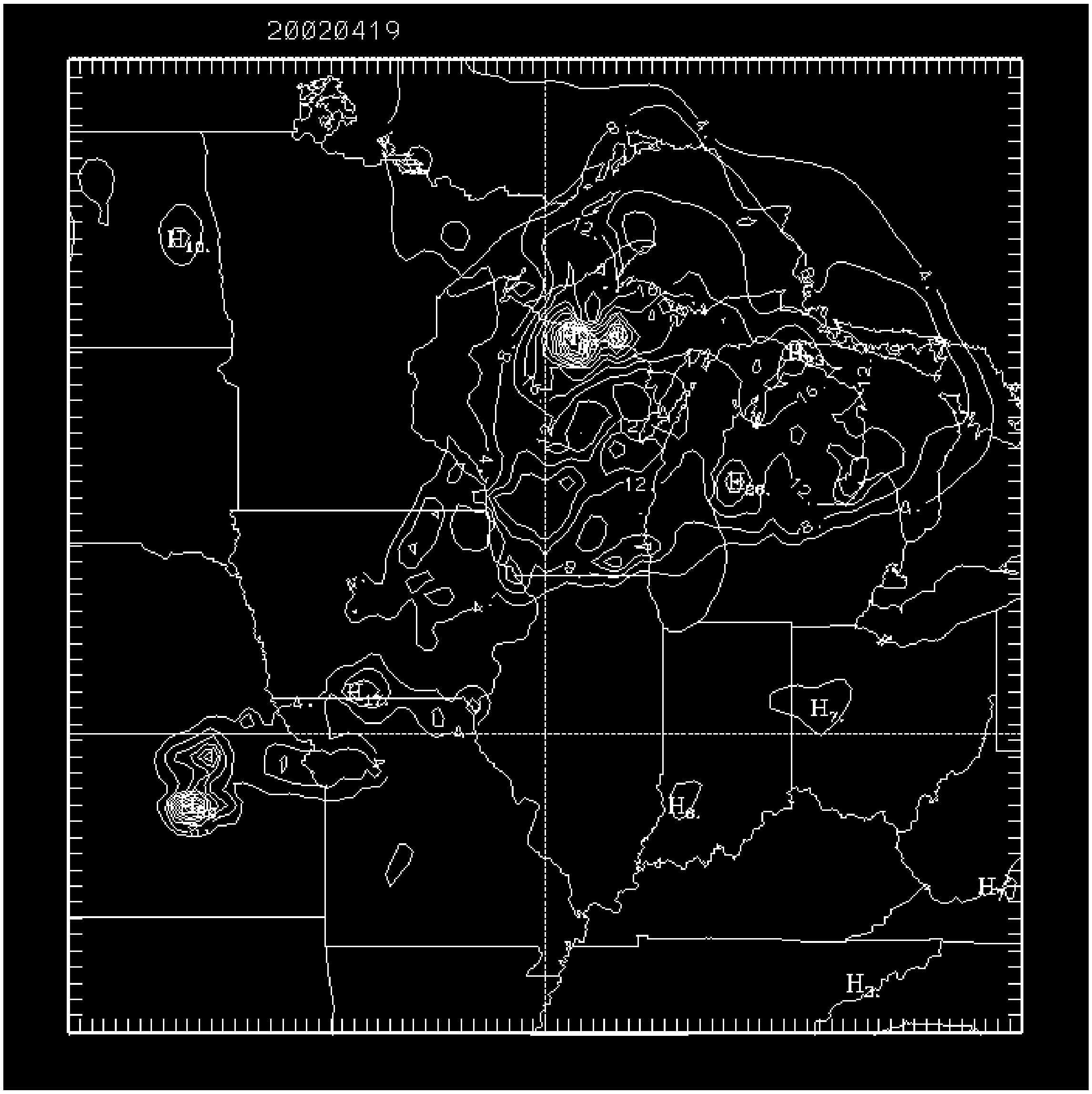
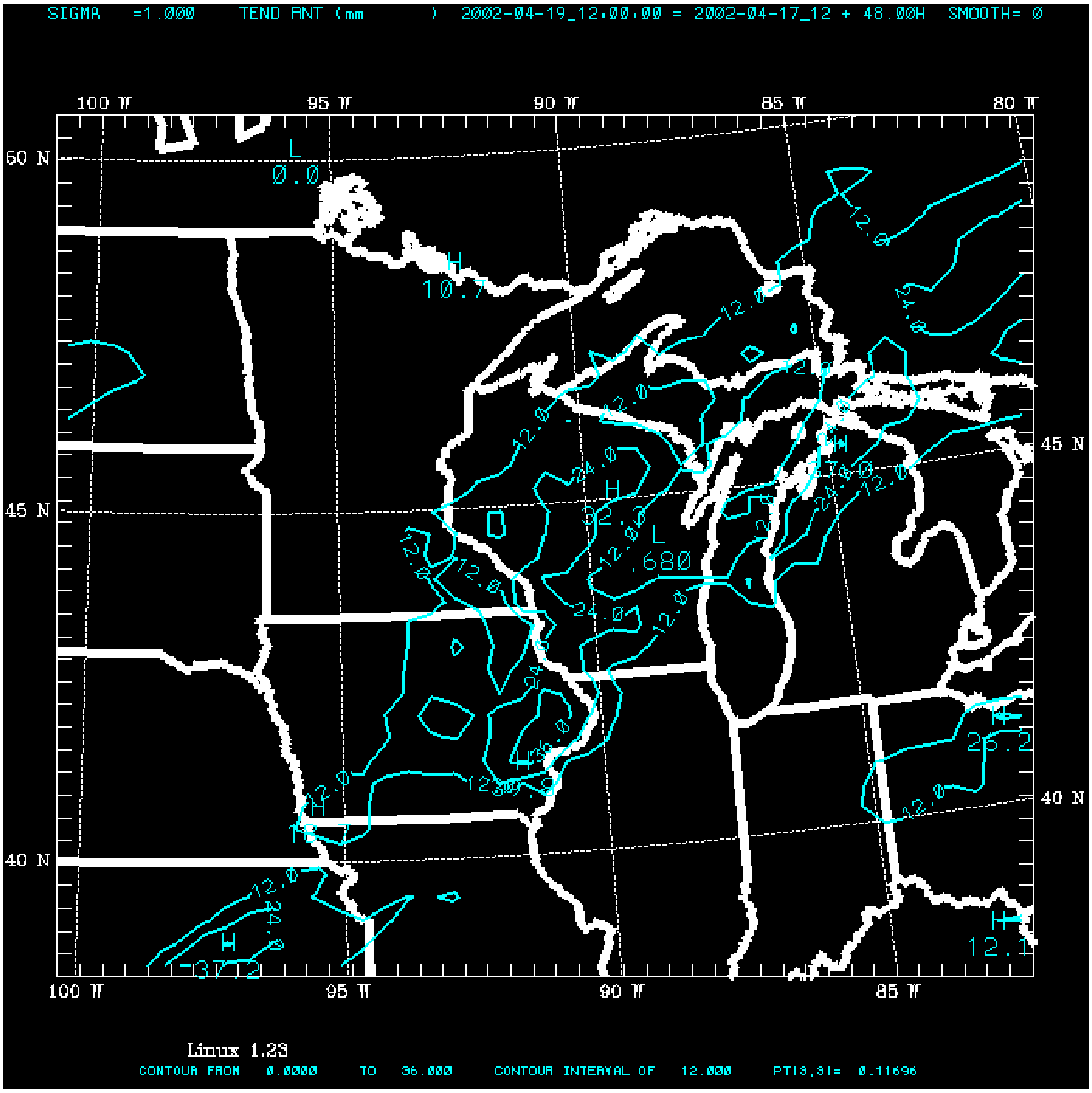


Figure 4-14. NCEP observed 24-hour daily rainfall total ending at 1200 UTC April 19, 2002 for Wisconsin

The unit is in mm, and the contour line interval is 4 mm.

Figure 4-15. MM5 with simple-ice moisture scheme predicted 24-hour daily rainfall total ending at 1200 UTC April 19, 2002 for Midwest in the 36 km grid

The unit is in mm, and the contour line interval is 12 mm.



During a lighter rainy day, both schemes perform reasonably, showing comparable rainfall patterns without too much difference. Maps show the 24-hour rainfall total each for the Reisner Graupel schemes, NCEP observations, and simple-ice schemes for April 21 and 22 over Wisconsin (Figures 4-16, 4-17, 4-18).

Figure 4-16. MM5 with Reisner Graupel moisture scheme predicted 24-hour daily rainfall total ending at 1200 UTC April 22, 2002 for Midwest in the 12 km grid

The unit is in mm, and the contour line interval is 4 mm.

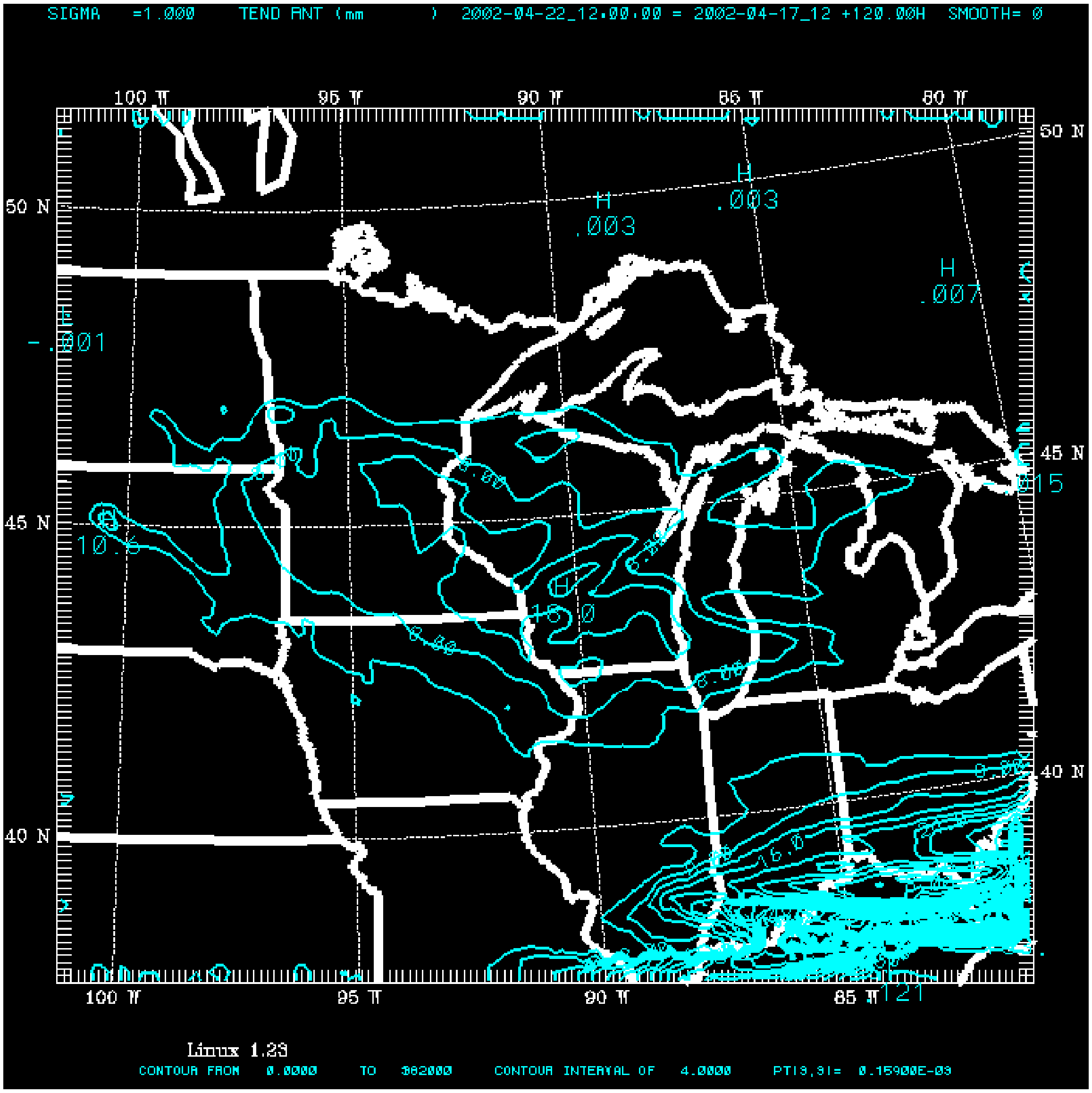


Figure 4-17. NCEP observed 24-hour daily rainfall total ending at 1200 UTC April 22, 2002 for Midwest

The unit is in mm, and the contour line interval is 4 mm.

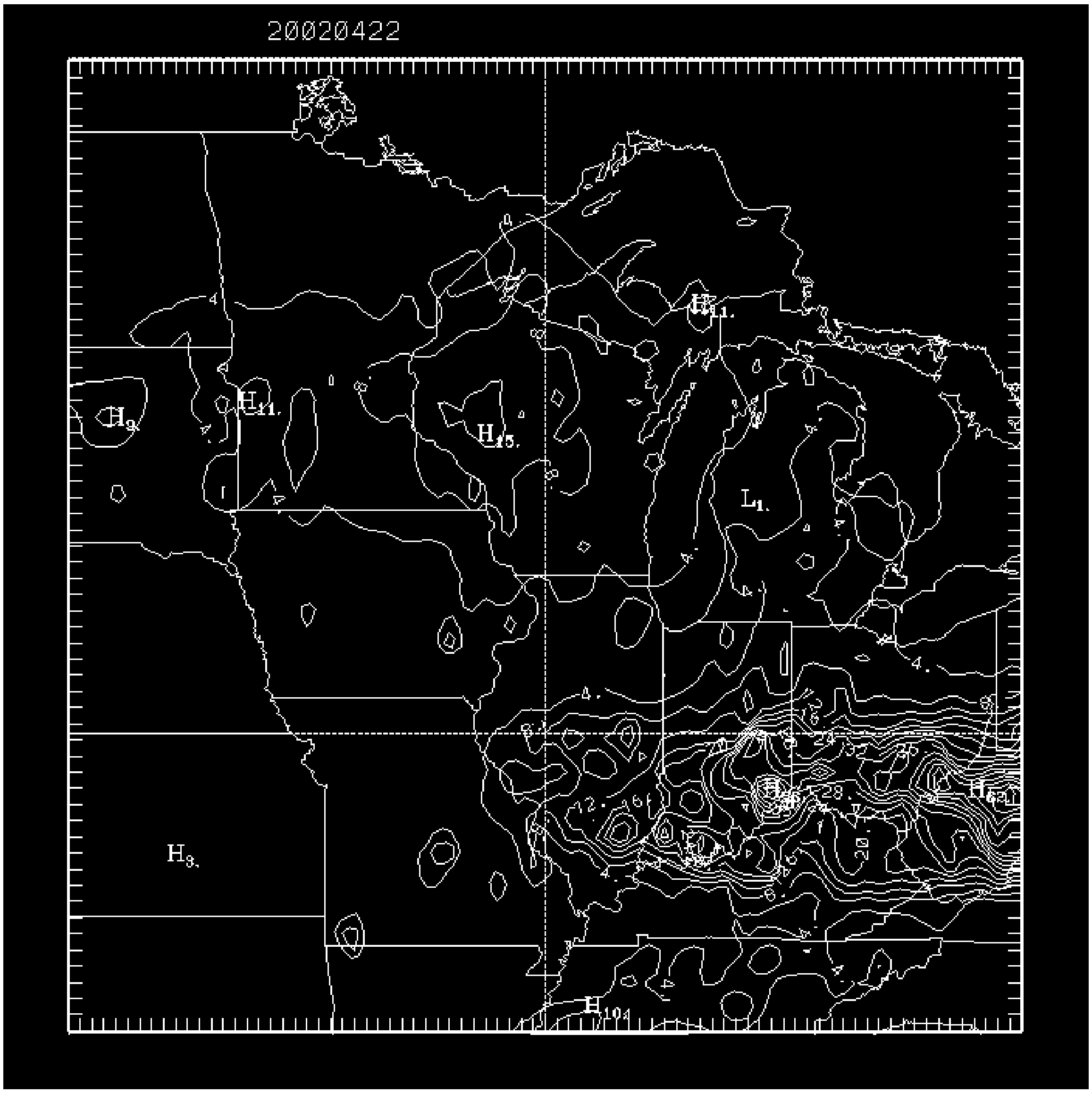
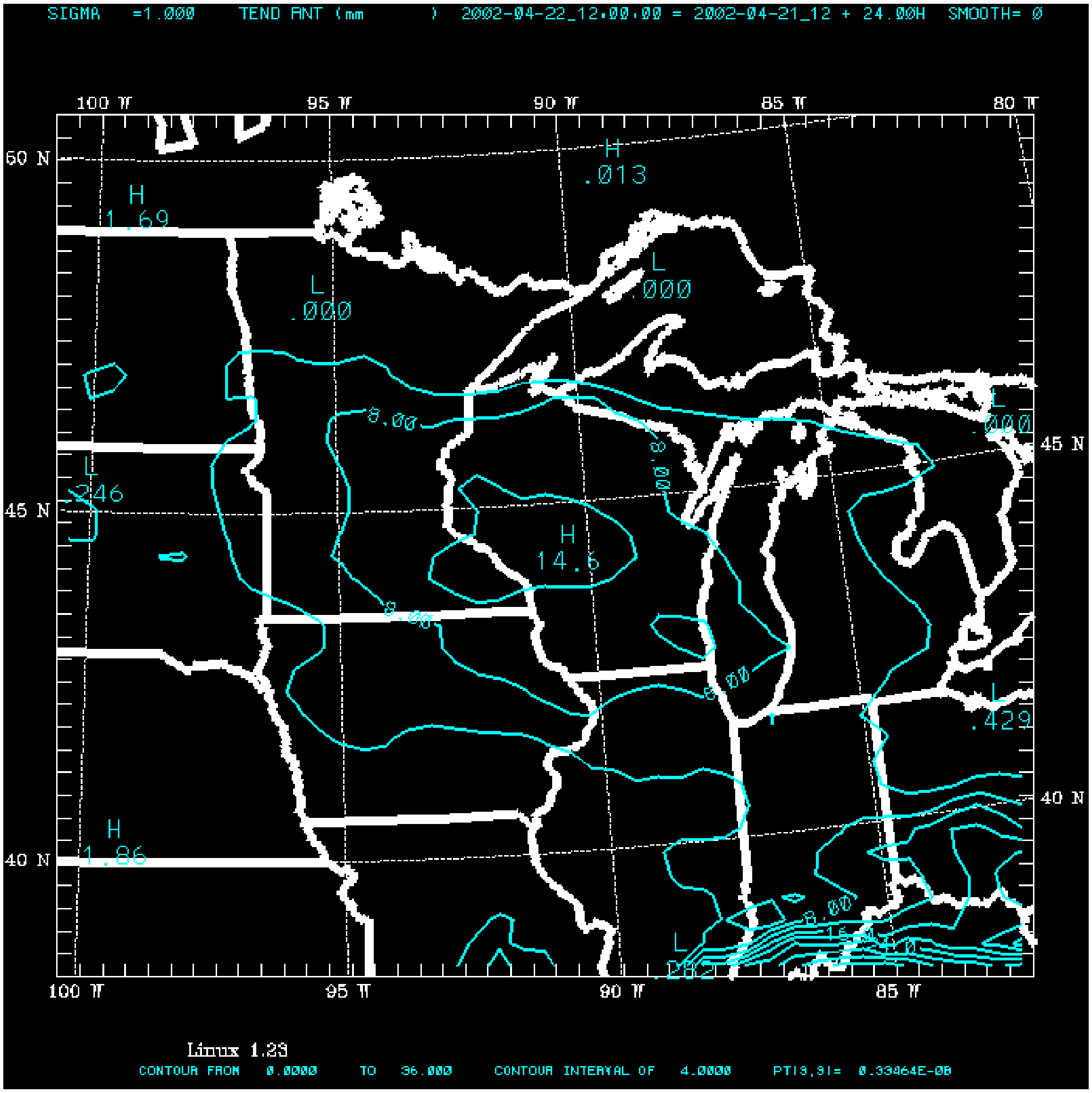


Figure 4-18. MM5 with simple-ice moisture scheme predicted 24-hour daily rainfall total ending at 1200 UTC April 22, 2002 for Midwest in the 36 km grid

The unit is in mm, and the contour line interval is 4 mm.



Statistical measures are applied to model results to evaluate the predicted surface temperatures and winds. The temperature and wind fields produced by the model are compared with the available observations by using METSTAT along with MM5 estimates (the first layer of MM5 output) and observations (NCAR ds472.0). Table 4-6 shows the daily surface temperature bias, temperature gross error, and wind speed index of agreement (IOA) for both schemes during the episode. The mean temperature bias and gross error for Reisner Graupel scheme are 0.03K and

2.32K respectively and –1.27K and 2.74K for the simple-ice scheme. This illustrates that the gross error and absolute value of the bias are both smaller for Reisner Graupel scheme. This indicates that the Reisner Graupel scheme provides a more accurate temperature field and confirms that the scheme indeed improves the surface temperature for the episode. The winds IOA for both schemes are very similar and no improvement is seen.

Table 4-6. METSTAT daily analyses during April 2002 episode
Temperature bias andgross error are in the unit of K. The April 2002 episode uses Reisner Graupel (RG)scheme and the annual 2002 episode uses the simple-ice (SI) scheme.

April 2002	Mean	4/12	4/13	4/14	4/15	4/16	4/17	4/18	4/19	4/20	4/21	4/22	4/23
Temp Bias (RG)	0.03	0.08	0.30	-0.12	-0.38	-1.04	-0.51	-0.76	0.38	1.01	0.53	0.95	-0.12
Temp Error (RG)	2.32	2.42	2.76	2.47	2.73	3.17	2.89	1.82	1.72	1.90	1.39	1.65	3.00
Wind Spd IOA (RG)		0.77	0.85	0.83	0.88	0.88	0.78	0.79	0.76	0.78	0.76	0.81	0.84
Annual 2002													
Temp Bias (SI)	-1.27	-1.70	-1.32	-1.29	-1.69	-2.48	-2.01	-1.89	-0.75	0.10	-0.36	-0.26	-1.55
Temp Error(SI)	2.74	2.73	2.98	2.70	3.19	3.79	3.24	3.00	2.33	2.01	1.41	2.00	3.50
Wind Spd IOA (SI)		0.77	0.87	0.84	0.88	0.87	0.77	0.84	0.77	0.80	0.81	0.85	0.87

In conclusion, the model with the Reisner Graupel scheme produces a reasonable meteorological field, including surface temperature and precipitation, in simulating the major rainfall system affecting Wisconsin. It also adequately reproduces the front-induced rainfall system location and the developing stages along with an overall improvement of the surface temperature field. It is important to note that the rainfall amount is only evaluated by 0.25-degree NCEP observations and this may not be fine enough for a thorough performance evaluation of an episode like this. The quantitative analysis of model rainfall remains a difficult task, and its solution is still essential for any complete model performance evaluation. However, based on the above analyses, it is believed that the MM5 with Reisner Graupel scheme realistically simulates the meteorology fields for our April 2002 episode, and the results are appropriate for our mercury deposition modeling application.

V. Emissions Inventory

A) Regional Emissions Model

Emissions for use in the photochemical model are processed by EMS2003. Files were created for a typical April weekday, Saturday and Sunday. The model ready surface file includes nonroad, mobile sources, other area, low-level point sources, and biogenics (for non-mercury species). The elevated point source file includes all point sources with an effective plume height above 50m. The latest version of EMS2003 is available from the LADCO website.

B) Non-Mercury Species Emissions Inventory

The emissions inventory for all non-mercury species was based on the Midwest Regional Planning Organization (MRPO) “BaseE” emissions. This inventory represents the following improvements from the baseD inventory (LADCO, 2003):

Spatial:	Revised/corrected surrogates for other area (including ammonia), nonroad, and mobile sources (BaseD used mostly farmland)
Temporal:	Revised/corrected profiles for point, other area, nonroad and mobile sources (BaseD used mostly “flat” temporal profiles)
	Profile for recreational marine based on Wisconsin data (BaseD used a flat day-of-week profile)
Mobile sources:	Corrected diesel emissions (BaseD did not include most of these emissions)
Ammonia:	Monthly and hourly livestock emissions based on new temporal profiles from Rob Pinder (Pinder)
	Dairy cow emissions based on Rob Pinder’s model (Pinder, Pekney, Strader, Davidson, & Adams, 2003)
	Monthly fertilizer application emissions derived using a consistent national profile
	Eliminated emissions for people and pets (dogs and cats)
Dust:	Emissions reduced to reflect the transportable fraction of fugitive dust
Fires:	Eliminated NEI and CMU fire emissions
Biogenics:	Used BIOME3 with updated meteorology and PAR value

A complete description of the development of the BaseE inventory can be obtained from LADCO (2003).

C) Mercury Emissions Inventory

The mercury emissions inventory for the continental United States, Canada, and Mexico was developed by the WDNR as follows.

United States

The 1999 National Air Toxics Assessment (NATA) Emissions Inventory based on the 1999 hazardous air pollutant (HAP) National Emissions Inventory (NEI) was selected as the foundation for the new mercury EI. This takes advantage of some quality assurance and data augmentation performed by EPA involving emission release point physical parameters (stack parameters), temporal profiles, and comparisons of annual and episodic emissions. Point and area source data based on the 1999 HAP NEI version 3-final was used. Nonroad and onroad mercury emissions were completely eliminated form the 1999 HAP NEI version 3-final due to a controversy concerning the magnitude of applied emission factors for these sources. There is no doubt that these sources merit inclusion in the mercury EI. As a result, nonroad and onroad data are based on the 1999 NEI version 3-draft. Additionally, for Wisconsin, Illinois, Minnesota and Michigan, the NATA EI data were consolidated with the 1999 Great Lakes States (GLS) EI data.

Mexico
The Mexican EI is based on a 1999 EI provided by the Council for Environmental Cooperation. The Mexican EI includes only point sources. Even though 1999 area source totals were available, insufficient data was presented for spatial allocation.

Canada
The Canadian EI is based on incomplete EIs for 1999 from the Ontario Ministry of the Environment (covering Ontario) and 1995 from Environment Canada (covering the rest of Canada.) The point source EI is based on voluntary reporting. For those who do report, many are granted confidentiality. As a result, a significant fraction of these point sources are relegated to the area source EI. The nonroad EI is limited to 1995 commercial marine outside of Ontario. The onroad EI is limited to Ontario.

Most of the emissions in the 1999 HAP NEI are reported as mercury and mercury compounds. These emissions were speciated using SCC cross reference tables in EMS2003 to elemental mercury, HG(0), oxidized mercury, HG(II), and particulate mercury, HG(p). Many of the emissions from utility boilers are reported in the 1999 HAP NEI already speciated based on information from USEPA's Information Collection Request (ICR) data that estimated the speciated mercury emissions from every U.S. coal-fired power plant in 1999.

Point and area source emissions for a typical spring weekday and the speciation profiles applied are summarized in Tables 5-1 and 5-2 respectively. Relative contributions for each of the inventory sectors are characterized in Figures 5-1 through 5-4. A summary of mercury emissions by state or province is included in Table 5-3. Elevated point source emissions for elemental mercury, divalent mercury and particulate mercury that were used in the modeling exercise are shown in Figures 5-5 through 5-7, respectively

Table 5-1. Point source mercury inventory

Category	**Reported Emissions (kg/day)**				**Speciation Profile (%)**			**Speciated Emissions (kg/day)**		
	HG	**HG(0)**	**HG(II)**	**HG(p)**	**HG(0)**	**HG(II)**	**HG(p)**	**HG(0)**	**HG(II)**	**HG(p)**
Utility/Ind/Comm Boilers Other Fuel	7.66	0.07	0.00	0.04	50	30	20	3.90	2.30	1.57
Utility/Ind/Comm Boilers Bituminous	28.25	5.76	0.17	3.20	54	44	2	21.02	12.60	3.76
Utility/Ind/Comm Boilers Anthrocite	0.12	0.00	0.00	0.00	56	42	2	0.07	0.05	0.00
Utility/Ind/Comm Boilers Lignite	1.62	0.84	0.03	0.17	75	24	1	2.06	0.42	0.18
Utility Boilers ICR (Fuel Not Specified)	0.00	52.82	3.33	43.86	NA	NA	NA	52.82	3.33	43.86
External Combustion Boilers	0.01	0.00	0.00	0.00	50	30	20	0.01	0.00	0.00

Category	Reported Emissions (kg/day)				Speciation Profile (%)			Speciated Emissions (kg/day)		
	HG	HG(0)	HG(II)	HG(p)	HG(0)	HG(II)	HG(p)	HG(0)	HG(II)	HG(p)
Utility/Ind/Comm Internal Combustion Engines	4.70	0.00	0.00	0.00	80	10	10	3.76	0.47	0.47
Industrial Processes	39.31	0.01	0.00	0.01	80	10	10	31.46	3.93	3.94
Primary & Secondary Metal Production	92.57	0.00	0.00	0.00	80	10	10	74.06	9.26	9.26
Mineral Products Process Heaters	0.01	0.00	0.00	0.00	50	30	20	0.00	0.00	0.00
Cement Manufacturing	4.24	0.00	0.00	0.00	74	25	1	3.14	1.06	0.04
Pulp and Paper	4.39	0.00	0.00	0.00	50	30	20	2.19	1.32	0.88
Industrial In-process Fuel Use: Coke	0.11	0.00	0.00	0.00	50	30	20	0.05	0.03	0.02
Industrial In-process Fuel Use: Other	0.50	0.00	0.00	0.00	80	10	10	0.40	0.05	0.05
Industrial In-process Fuel Use: Bituminous	0.11	0.00	0.00	0.00	54	44	2	0.06	0.05	0.00
Petroleum and Solvent Evaporation	0.13	0.00	0.00	0.00	80	10	10	0.11	0.01	0.01
Government/Commercial/Institutional/Industrial Landfill	2.21	0.00	0.00	0.00	100	0	0	2.21	0.00	0.00
Government/Commercial/Institutional/Industrial Incineration	10.19	0.00	0.00	0.00	24	75	1	2.45	7.64	0.10
Government/Commercial/Institutional/Industrial Medical Waste Incineration	10.49	0.00	0.00	0.00	4	95	1	0.42	9.97	0.10
Industrial Hazardous Waste Incineration	13.74	0.00	0.00	0.00	58	20	22	7.97	2.75	3.02
Canada Highway Mobile Sources	0.45	0.00	0.00	0.00	90	10	0	0.40	0.04	0.00
Canada Off-Highway Mobile Sources	0.88	0.00	0.00	0.00	90	10	0	0.79	0.09	0.00
Canada Commercial Pesticide Application	0.40	0.00	0.00	0.00	100	0	0	0.40	0.00	0.00
Canada Medical Waste Incineration	0.00	0.00	0.00	0.00	33	50	17	0.00	0.00	0.00
Miscellaneous Sources Receiving Defaults	15.00	0.00	0.00	0.00	80	10	10	12.00	1.50	1.50
Totals:	237.08	59.51	3.54	47.27				221.73	56.88	68.78

Table 5-2. Area source mercury inventory

Category	Reported Emissions (kg/day)		Speciation Profile (%)			Speciated Emissions (kg/day)		
	HG	HGCMP	HG(0)	HG(II)	HG(p)	HG(0)	HG(II)	HG(p)
Ind/Comm/Res Fuel Comb Other	1.98	0.16	50	30	20	0.99	0.59	0.40
Ind/Comm/Res Fuel Comb	0.25	0.01	54	44	2	0.14	0.11	0.01

Category	Reported Emissions (kg/day)		Speciation Profile (%)			Speciated Emissions (kg/day)		
	HG	HGCMP	HG(0)	HG(II)	HG(p)	HG(0)	HG(II)	HG(p)
Bituminous								
Ind/Comm/Res Fuel Comb Anthrocite	0.03	0.00	56	42	2	0.01	0.01	0.00
Off-Highway Mobile Sources	24.66	21.77	90	10	0	22.19	2.47	0.00
Highway Mobile Sources	56.73	56.24	90	10	0	51.06	5.67	0.00
Industrial Processes	9.99	0.47	80	10	10	7.99	1.00	1.00
Solvent Utilization	0.00	0.00	100	0	0	0.00	0.00	0.00
On-Site Incineration	0.01	0.00	24	75	1	0.00	0.01	0.00
Open Burning	0.07	0.00	100	0	0	0.07	0.00	0.00
Landfills	0.22	0.00	100	0	0	0.22	0.00	0.00
TSDFs	0.00	0.00	100	0	0	0.00	0.00	0.00
Scrap & Waste Materials	0.00	0.00	100	0	0	0.00	0.00	0.00
Agricultural Production	3.45	0.01	100	0	0	3.45	0.00	0.00
Misc. Area Source Combustion	0.00	0.00	100	0	0	0.00	0.00	0.00
Cremation and Pathological Incineration	0.69	0.13	33	50	17	0.23	0.34	0.12
Fluorescent Lamp Breakage	2.51	0.01	100	0	0	2.51	0.00	0.00
Totals:	21.79	78.80				88.87	10.20	1.52

Figure 5-1. Spring weekday elemental mercury, Hg(0), by source type

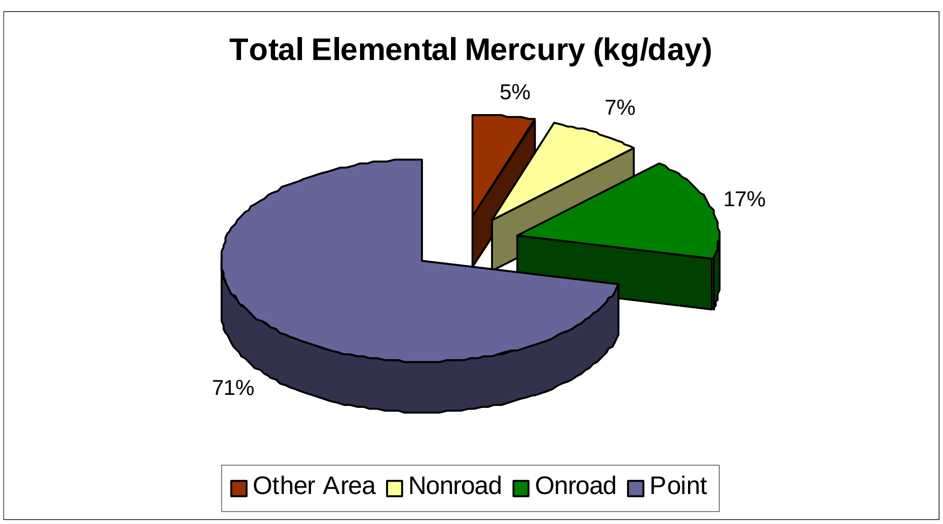


Figure 5-2. Spring weekday divalent mercury, Hg(II), by source type

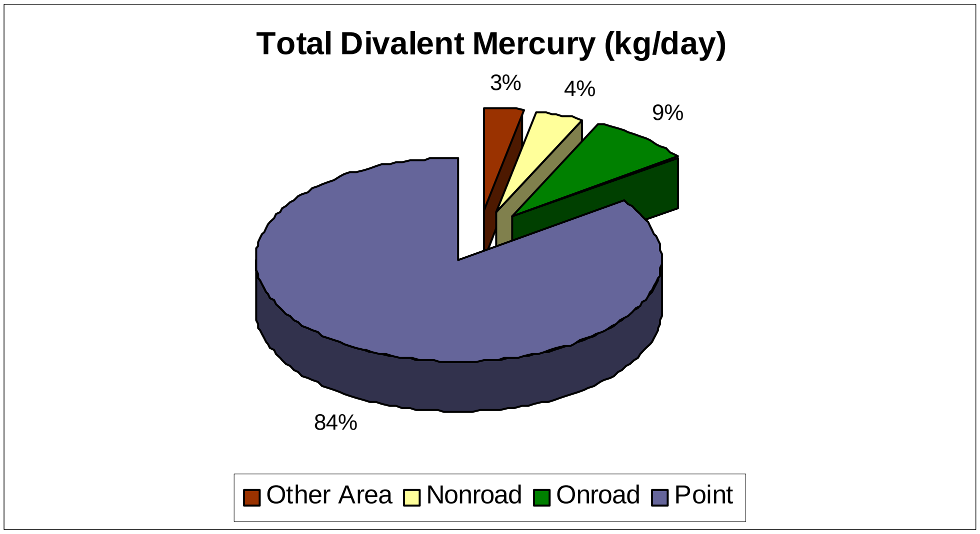


Figure 5-3. Spring weekday particulate mercury, Hg(p), by source type

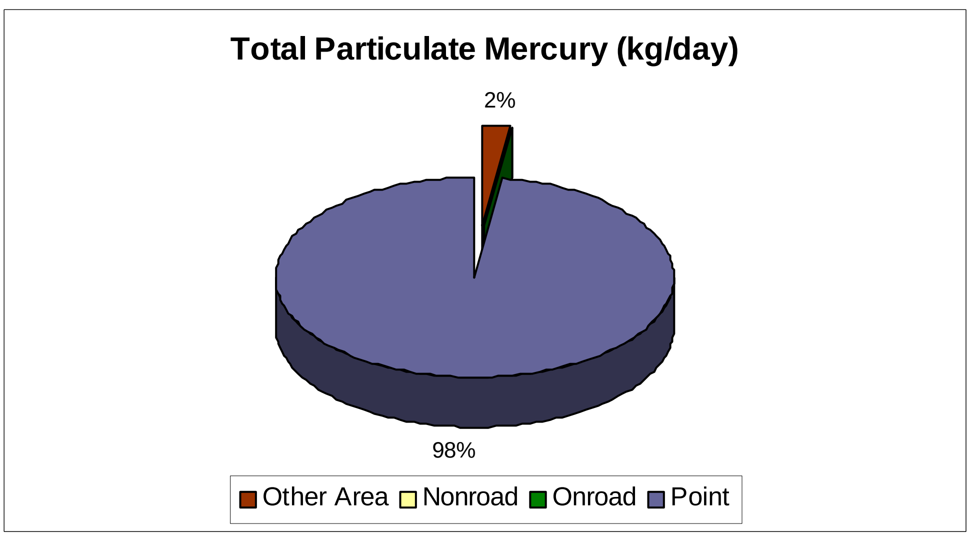


Figure 5-4. Spring weekday total mercury by source type

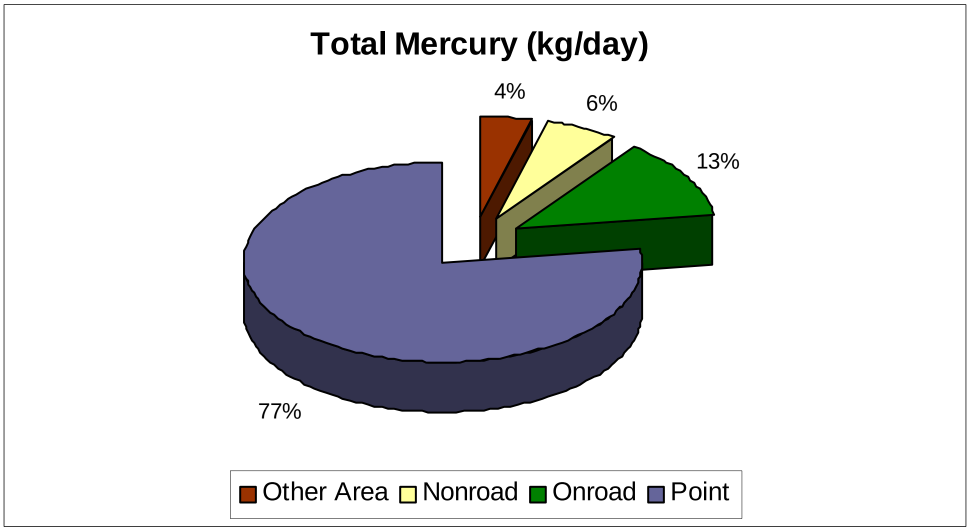


Table 5-3. Summary of total mercury by state and province

Country	FIPS State ID	State Name	Hg Point kg/day	Hg Other Area kg/day	Hg Nonroad kg/day	Hg Onroad kg/day
USA	1	Alabama	9.14	0.15	0.31	1.19
USA	4	Arizona	2.18	0.14	0.30	1.07
USA	5	Arkansas	2.41	0.08	0.40	0.80
USA	6	California	11.12	9.94	2.94	0.49
USA	8	Colorado	1.31	0.11	0.39	0.87
USA	9	Connecticut	0.73	0.11	0.15	0.63
USA	10	Delaware	1.77	0.03	0.06	0.20
USA	11	District of Columbia	0.00	0.01	0.02	0.06
USA	12	Florida	8.05	0.61	0.86	3.04
USA	13	Georgia	6.63	0.31	0.52	2.37
USA	16	Idaho	1.89	0.20	0.20	0.38
USA	17	Illinois	21.46	0.36	1.24	2.26
USA	18	Indiana	9.98	0.18	0.71	1.77
USA	19	Iowa	2.61	0.10	0.86	0.79
USA	20	Kansas	2.89	0.09	0.74	0.70
USA	21	Kentucky	8.41	0.11	0.39	1.25
USA	22	Louisiana	5.82	0.11	0.63	1.06
USA	23	Maine	0.45	0.65	0.08	0.26
USA	24	Maryland	8.11	0.15	0.25	1.09
USA	25	Massachusetts	1.74	0.20	0.48	1.06
USA	26	Michigan	8.33	0.31	0.63	2.23
USA	27	Minnesota	5.07	0.39	0.84	1.28

Country	FIPS State ID	State Name	Hg Point kg/day	Hg Other Area kg/day	Hg Nonroad kg/day	Hg Onroad kg/day
USA	28	Mississippi	2.35	0.07	0.33	1.10
USA	29	Missouri	4.34	0.16	0.68	1.62
USA	30	Montana	1.40	0.03	0.36	0.29
USA	31	Nebraska	1.23	0.05	0.65	0.48
USA	32	Nevada	29.08	0.05	0.17	0.40
USA	33	New Hampshire	0.46	0.07	0.05	0.31
USA	34	New Jersey	2.41	0.50	0.35	1.33
USA	35	New Mexico	2.87	0.05	0.15	0.60
USA	36	New York	4.73	1.00	0.87	2.76
USA	37	North Carolina	7.09	0.22	0.52	2.19
USA	38	North Dakota	3.09	0.03	0.63	0.21
USA	39	Ohio	12.21	0.33	0.94	2.47
USA	40	Oklahoma	3.02	0.10	0.41	1.07
USA	41	Oregon	6.32	0.24	0.32	0.89
USA	42	Pennsylvania	19.02	0.33	0.63	2.47
USA	44	Rhode Island	0.37	0.03	0.03	0.16
USA	45	South Carolina	3.76	0.12	0.25	1.19
USA	46	South Dakota	0.16	0.02	0.44	0.24
USA	47	Tennessee	5.57	0.16	0.44	1.57
USA	48	Texas	20.00	0.56	1.38	4.74
USA	49	Utah	2.45	0.07	0.29	0.47
USA	50	Vermont	0.00	0.02	0.04	0.19
USA	51	Virginia	3.69	0.20	0.45	1.76
USA	53	Washington	1.99	0.16	0.50	1.18
USA	54	West Virginia	8.04	0.05	0.14	0.54
USA	55	Wisconsin	6.51	0.25	0.52	1.46
USA	56	Wyoming	2.65	0.02	0.12	0.22
Canada	10	Newfoundland	0.14	0.00	0.00	0.00
Canada	11	Prince Edward Island	0.42	0.00	0.00	0.00
Canada	12	Nova Scotia	1.31	0.00	0.00	0.00
Canada	13	New Brunswick	0.96	0.00	0.00	0.00
Canada	24	Quebec	4.66	0.00	0.00	0.00
Canada	35	Ontario	2.04	0.00	0.00	0.00
Canada	46	Manitoba	4.21	0.00	0.00	0.00
Canada	47	Saskatchewan	1.26	0.00	0.00	0.00
Canada	48	Alberta	2.00	0.00	0.00	0.00
Canada	59	British Columbia	6.65	0.00	0.00	0.00
Mexico	15	All States	48.84	0.00	0.00	0.00
Totals:			347.39	19.20	24.66	56.73

Figure 5-5. Elevated point source emissions of Hg(0) for the CAMx coarse grid for a Spring weekday

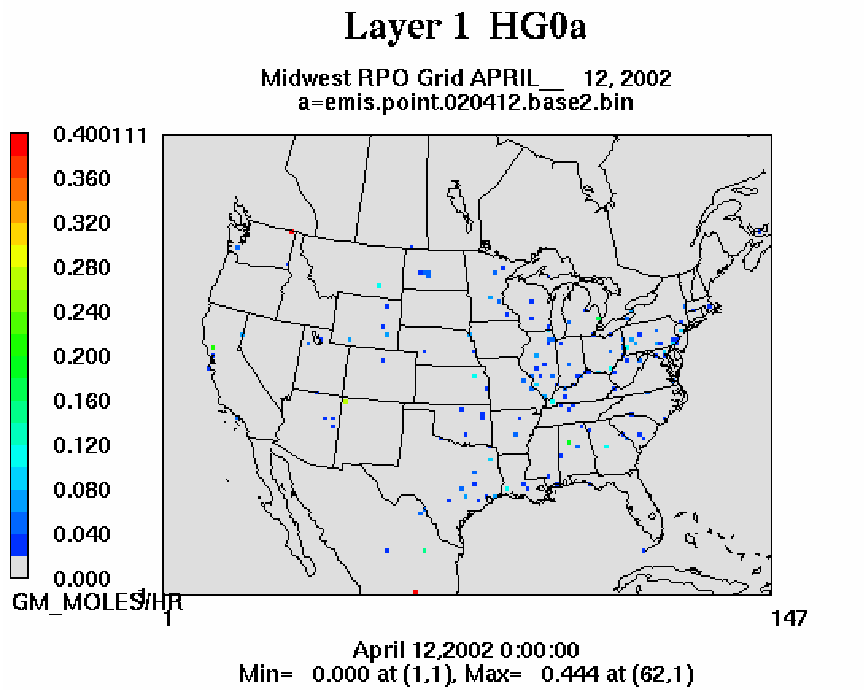


Figure 5-6. Elevated point source emissions of Hg(II) for the CAMx coarse grid for a Spring weekday

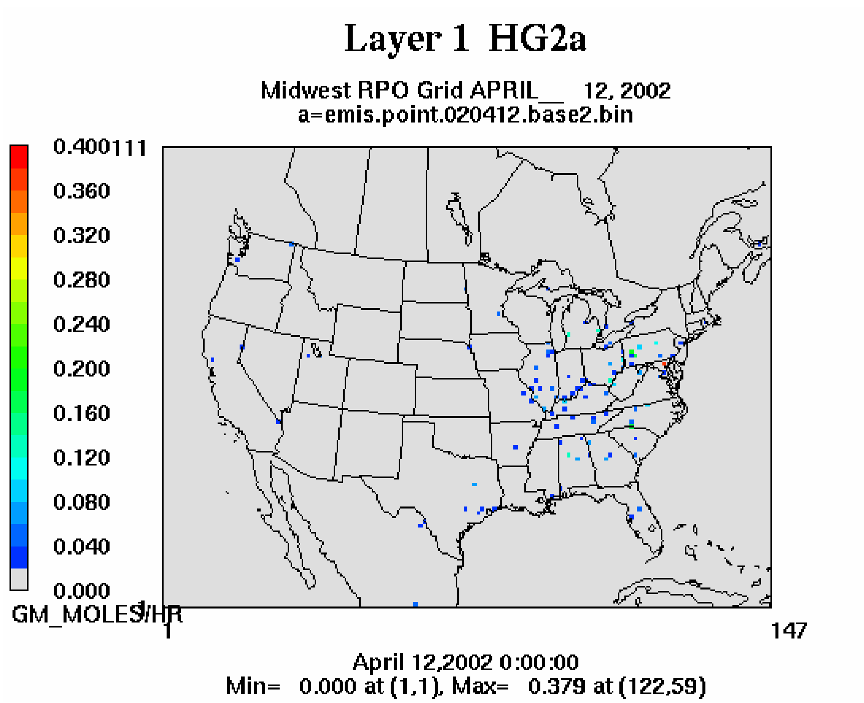
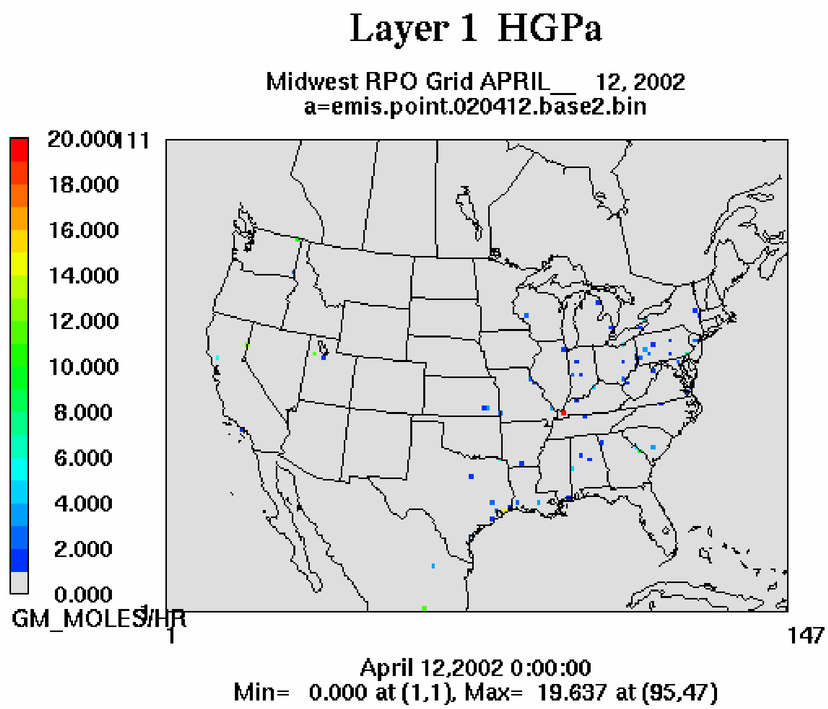


Figure 5-7. Elevated point source emissions of Hg(p) for the CAMx coarse grid for a Spring weekday



VI. Model System Development Results

The episodic mercury simulation was for April 12, 2002 to April 23, 2002. The deposition monitoring at the MDN sites was for the period April 16 through April 22. Monitoring at the Devil's Lake site began on April 15. Selected model options were:

PPM advection solver
CMC chemistry solver
No plume-in-grid sub-model
Dry and wet deposition enabled

Also, the fine grid nesting option was used. Meteorological data for the 36 km and 12 km grids were used. Only the 36 km area emissions file was used. The CAMx model interpolated these emissions to the 12 km grid so no specific fine grid file was created. There is no fine grid file for point source emissions as they are located according to their given coordinates.

The CAMx model was initially run with a 36 km coarse grid (17 layers) structure in place and for the period from March 1 through April 30, 2002. Additionally, an initial meteorological data set from MM5 was from a run with the "simple-ice" moisture scheme. Subsequently, CAMx was run in the nested 36 km/12 km configuration and MM5 was run with the Reisner moisture scheme. This was done to determine the model performance when a fine grid and a more sophisticated moisture scheme are used to help resolve cloud physics and precipitation. Figures 6-1 through 6-3 show three plots for hour 19 on April 18, 2002. This hour matches the 00Z April 19 synoptic scale surface plot in Figure. 3-5. The mercury deposition plots are for three different grid schemes. Figure 6-1 is for the 36 km grid when the model was run with only the 36 km coarse grid and the simple-ice scheme. Figure 6-2 is also for a 36 km grid but when the model is run in the 36 km/12 km setup and the Reisner scheme. The final plot, Figure. 6-3, is for the 12 km fine grid with the Reisner scheme.

For the 36 km grid (simple-ice) results, at first glance, mercury deposition seem to match the radar echoes. The mercury, Hg(II) and Hg(p), wet deposition pattern outlines the frontal boundary that moved across the Midwest. The wet deposition indicated across Wisconsin is occurring in an area of radar rainfall echoes. Mercury deposition occurs along the front from Wisconsin to northeast Kansas. Further to the southwest, across the remainder of Kansas, Oklahoma, and the Texas panhandle, deposition is depicted to occur but the radar plot indicates this area to be free of echoes. Thus making the deposition questionable in this area.

The 36 km deposition results from the 36 km /12 km configuration also show deposition along the frontal boundary over Wisconsin. However, there is greater coverage over southern Wisconsin and the Great Lakes area in general. This pattern is a good match to the radar echoes at this time. This grid configuration seems to capture the lack of deposition (radar echoes) over the southern Plains and seems to better depict the area of rain over southwest Texas.

12 km fine grid results give more definition to the deposition (rain) area in the Midwest. Most notable is the "dry" region over east-central Wisconsin to southern Wisconsin. This area is

bounded by deposition to the northwest and near the Wisconsin-Illinois border. Close inspection of the synoptic chart shows the radar echoes are a very close match to the deposition area over Wisconsin. Inclusion of the fine grid has greatly improved the match between deposition area and the area of rainfall echoes.

Figure 6-1. Wet deposition of mercury on 36 km grid (simple-ice)

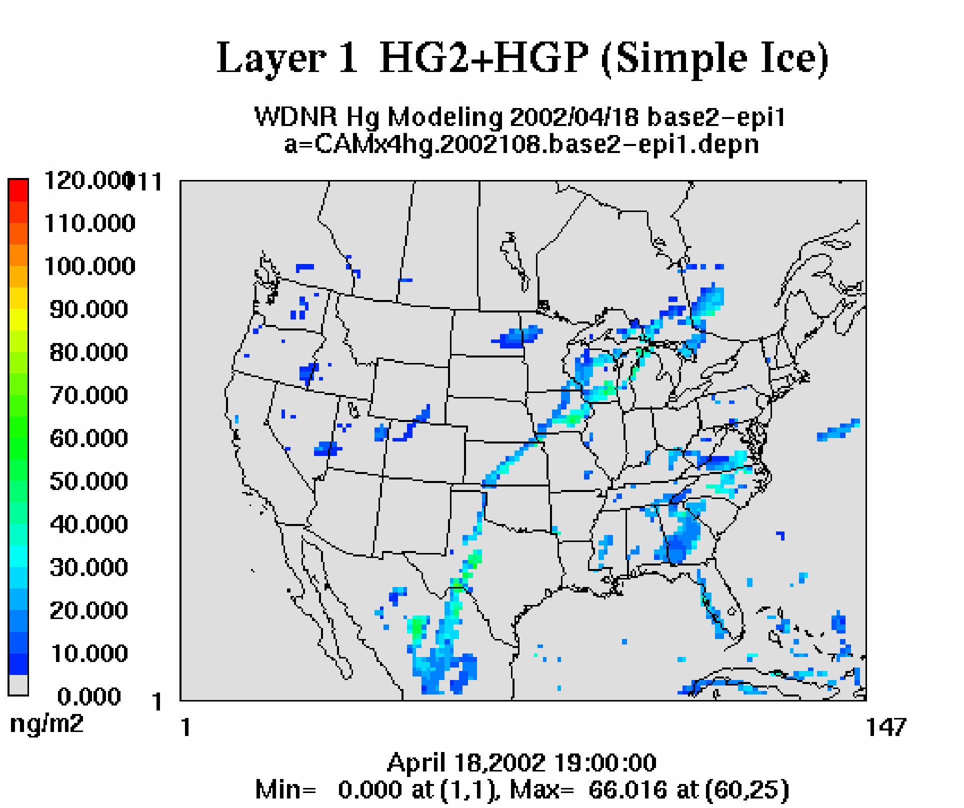


Figure 6-2. Wet deposition of mercury on 36 km grid (Reisner)

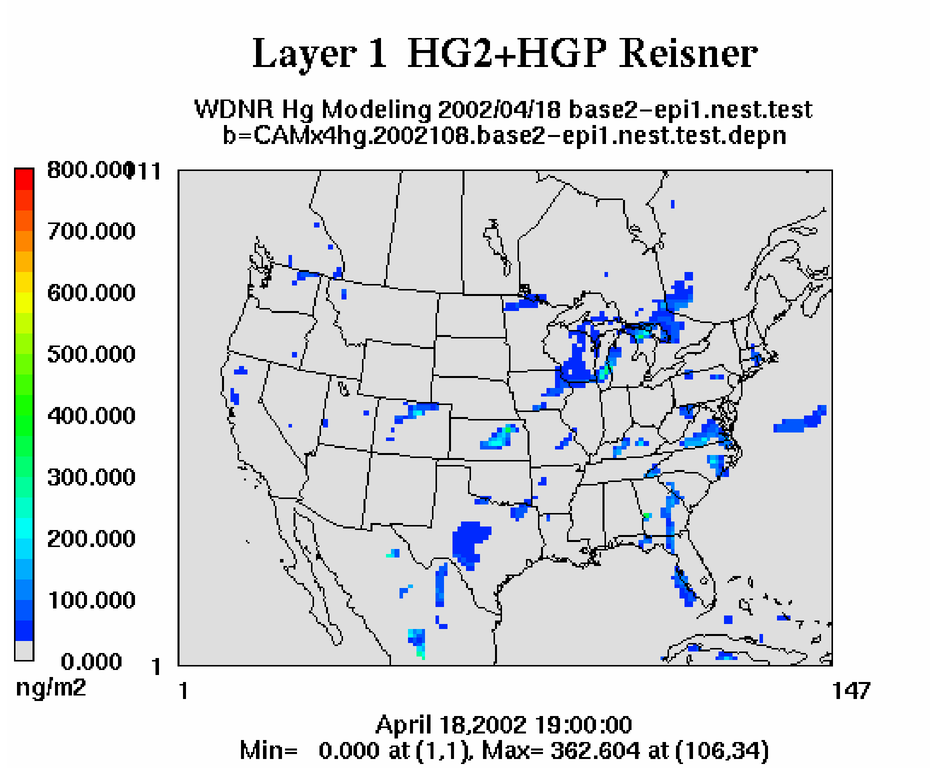
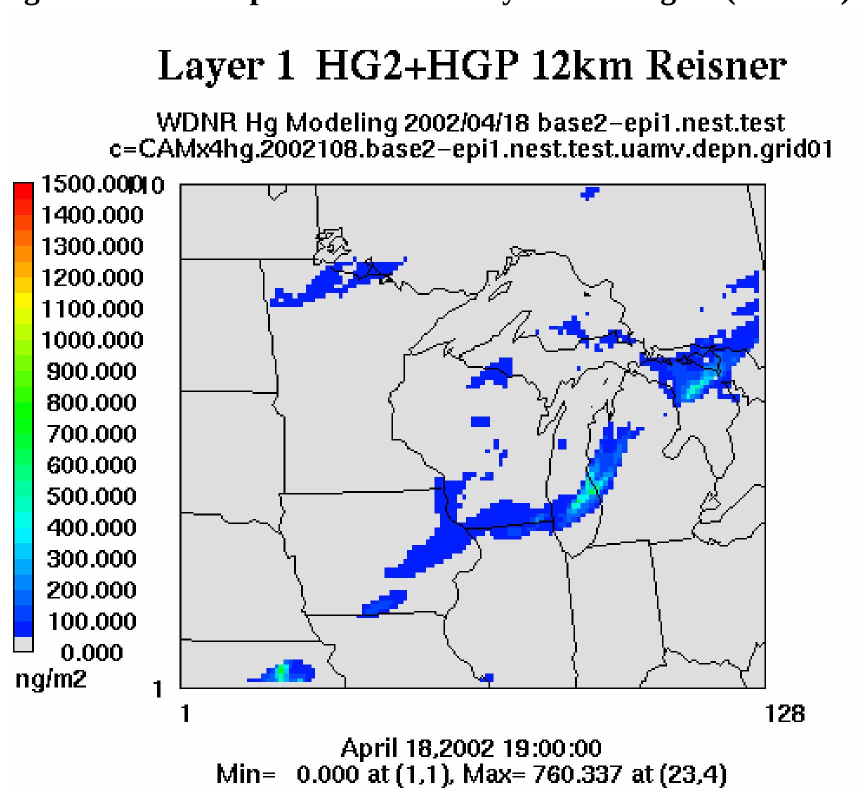
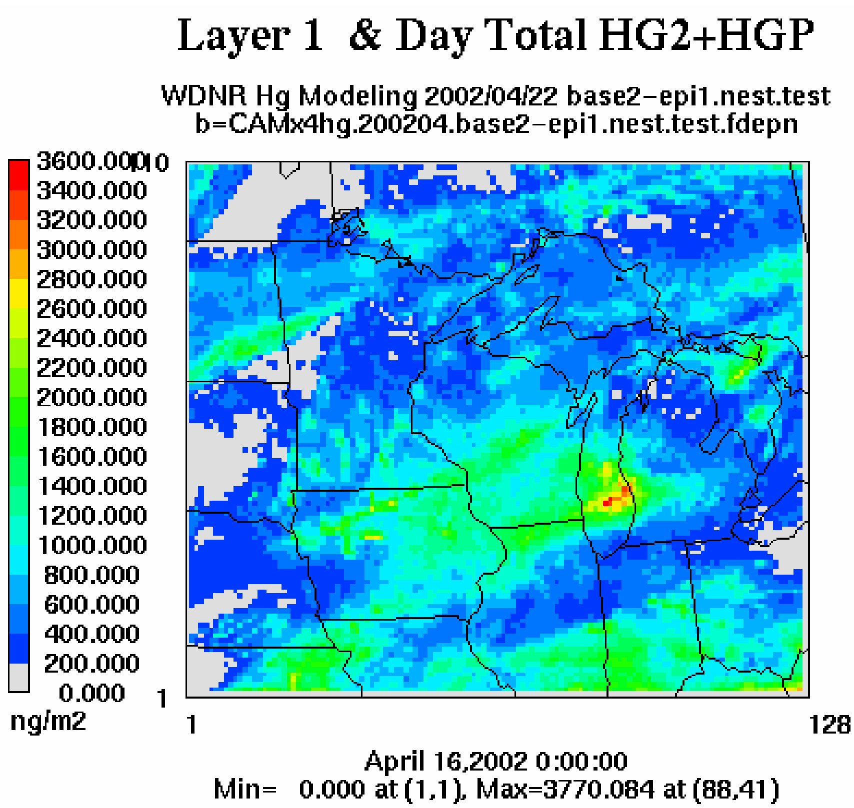


Figure 6-3. Wet deposition of mercury on 12 km grid (Reisner)



Modeled mercury wet deposition amounts for the episode (7 day total) are shown in Figure 6-4. Deposition of elemental mercury is not included because it was set to zero by setting a very small Henry's constant for Hg(0) as discussed in ENVIRON's report (Yarwood, 2003). Essentially, Hg(0) is only slightly soluble and is not removed readily by wet deposition. Since the MDN sites measure deposition on a 7 day cycle the hourly predicted deposition values were added together for the period of April 16 through April 22. This would allow a direct comparison of modeled to measured deposition values. There are two main area of deposition across Wisconsin, one "plume" of deposition is predicted along the Wisconsin-Illinois border extending northeastward over Lake Michigan. The highest predicted wet deposition, for this period, is found within this "plume" over Lake Michigan. This band also covers the Lake Geneva monitoring site, where high deposition values were recorded.

Figure 6-4. Total 7 day wet deposition on 12 km grid



Another main area of deposition runs west to east across the south-central part of Wisconsin. This band is just to the northwest of the Devil's Lake site. The second highest value for this 7-day episode was measured at the Devil's Lake site. It is important that the model is predicting the highest mercury deposition at, or very near, these 2 monitoring sites.

The third monitoring site with high deposition measurements (Popple River) is located in the northeastern Wisconsin. High values are not predicted actually at the Popple River site but there is a band of elevated deposition values predicted just to the northwest that range from 800-1000 ng/m2. Based on the 7-day totals it is encouraging to see the CAMx model predicting deposition in a spatial pattern that matches the observations.

Model results, for this episode, for the 12 MDN sites, along with observed values, are shown in Table 6-1. This table lists the deposition values that are predicted for the grid cell containing the individual monitoring site. Also, the table lists the predicted deposition values for a given grid structure (36 km or 36 km/12 km) and a given moisture scheme (simple-ice or Reisner). Generally, the 36 km, simple-ice scheme yielded results that were much lower than the observations. This is because this scheme was not generating precipitation in the locations or at the intensities indicated by radar. The 36 km, Reisner scheme generated closer observation/prediction pairs, especially at the Wisconsin sites. Predictions at four of the five sites were very close to the observations. The biggest discrepancy was at the Popple River site. But as mentioned earlier, there was an area of predicted high values just to the northwest of this site.

Table 6-1. Total wet mercury deposition predicted (ng/m^2) in the grid cell containing the monitoring site

Site Name	**36 km (simple ice)**	**36 km (Reisner)**	**12 km (Reisner)**	**Actual (ng/m^2)**
Wisconsin				
Brule River	71	510	526	418
Trout Lake	174	862	992	895
Popple River	221	671	599	1164
Devil’s Lake	599	1132	906	1124
Lake Geneva	440	1503	1506	1100
Minnesota				
Lamberton	304	1260	572	277
Fernberg	325	739	608	125
Camp Ripley	512	386	299	125
Indiana				
Indiana Dunes	655	561	396	899
Roush Lake	417	841	530	263
Clifty Falls	788	1055	1279	867
Illinois				
Bondville	600	1084	975	273

For the Wisconsin sites, the 36 km-Reisner scheme also predicted the lowest deposition at the site (Brule River) where the lowest deposition was actually recorded.

The 36 km-Reisner scheme performance was less encouraging at the remaining 7 Midwest sites. Results ranged from over-prediction at the Lamberton site to underprediction at the Indiana Dunes site.

The original hypothesis was that the inclusion of a fine grid (12 km-Reisner scheme) would lead to improved mercury deposition because of a better resolution of the convective elements in the MM5 model. While the fine grid may have given better definition to the areas of rainfall its impact on mercury deposition yielded mixed results. At eight of the twelve monitoring sites predicted mercury deposition values decreased compared to the values predicted on the 36 km grid. Three sites increased and one remained essentially unchanged (Lake Geneva). For this episode, the use of a fine grid did not lead to better mercury deposition results than the 36 km grid.

VII. Peer Review

As part of the advancement of a regional modeling system that can be used for mercury, WDNR contracted with Alpine Geophysics to provide a peer review of the 2002 annual simulation performed by ENVIRON during CAMx development (Yarwood, 2003). Alpine delivered their final report to WDNR, *Scientific Peer-Review of the HgCAMx Atmospheric Mercury Model and its Application to the 2002 Annual Cycle*, on April 16, 2004. The full report is available in Appendix B. Overall, Alpine's review was favorable. Many of the improvements that are recommended are to be expected during the initial applications of a new modeling system. The comments from Alpine's report that recommend action are listed here with WDNR's response as it relates to the subsequent April 2002 episodic modeling.

Comment 1:

> "There is a 15% difference in the total national mercury mass between the summaries prepared by ENVIRON and WDNR."

Response:

> The discrepancy comes from comparing the mercury mass listed in the ENVIRON report and the document "WDNR Mercury Emissions Inventory Development" (Appendix A). The inventory given to ENVIRON was based on the National Emissions Inventory (NEI) version 3 draft. The final inventory as reported in the WDNR report is based on the final version 3 of the NEI.

Comment 2:

> "The base emissions data pertain to 1999 while the year actually modeled was 2002."

Response:

> WDNR agrees that this is a deficiency in the modeling exercise. At the present time there is no 2002 inventory or projection guidance available.

Comment 3:

> "An annual emissions inventory was not used to capture the seasonal cycles in mercury deposition….only three 'representative' days from two seasons were modeled."

Response:

> WDNR agrees that this is a deficiency. Since the ENVIRON modeling exercise, WDNR has prepared three representative days for each month of the year, a practice consistent

with MRPO modeling exercises. For our April episodic modeling, three representative days (weekday, Saturday, and Sunday) for April were used.

Comment 4:

"The non-mercury emissions inventory should be updated to utilize the "Base E" inventory rather than the outdated "Base D" inventory."

Response:

At the time of the ENVIRON modeling exercise, "Base D" was the most currently available non-mercury inventory. When "Base E" was made available we immediately started using it for our episodic modeling. WDNR would recommend that any modeling be done with the most recently available inventory that has received peer review.

Comment 5:

"Conduct a review of the default application of the speciation profiles to determine if they are appropriate."

Response:

WDNR did review the default application of speciation profiles. In almost all cases the category receives the default for point or area sources. However, categories receiving a default value have been added to the speciation processors for clarity.

Comment 6:

"The precipitation rates used in the HgCAMx model are much higher than observations (a factor of 2-3) and the performance is markedly inferior to the MM5 performance in comparison to the EPA annual modeling for 2001. ….Since mercury wet deposition is proportional to rainfall rate, this large error casts doubt on the present suitability of the HgCAMx modeling system and the 2002 episode as a credible planning tool for estimating wet mercury deposition."

Response:

According to our analysis, the annual rainfall predicted by MM5 is at most only a factor of 1.7 higher than the observations. The methodology used to approximate the rainfall was not perfect. The MM5 rainfall total obtained was not based on the actual rainfall predicted by the model, instead, the result was based on the intermediate 3D rain field used by the model without considering the other microphysics conditions like the vertical winds. Since all the rain droplets in the 3D rain fields are not precipitable, this method of estimating the rainfall total is questionable. When rain droplets descend in the cloud, some of them may fall to the surface as rain and some of them may break up during the descent and become smaller droplets (cloud droplets). These droplets stay in the air indefinately depending on the local wind direction (up or down) and collision probability with other rain drops. This could partially explain why the rainfall total was so high.

Additionally, the CAMx model developer has developed an alternative wet deposition option that would be driven by surface precipitation data.

Comment 7:

"Strengthening the model performance testing procedures by inclusion of other gas-phase and secondary aerosol species, and possibly including performance testing aloft with data

> from WDNR's 2002 aircraft flights is viewed as a (sic) essential next step in building confidence that the HgCAMx tools is (sic) suitable for regulatory air quality impact analyses. The present evaluation suggests that the model is not yet suitable as a tool for supporting public decision making."

Response:

> WDNR agrees that the model needs more testing and evaluation to develop confidence in the model results. Policy maker's should not rely solely on results from the CAMx model in making decisions related to Hg control.

VIII. Summary and Conclusions

The objective of this study was to apply the recently developed CAMx to an episodic mercury deposition event during April 2002. The major modification to CAMx was the addition of a new chemistry module to treat the gas and aqueous-phase chemistry of the mercury species.

A modeling database was developed to test and evaluate the CAMx model. The modeling domain was the 36 km National RPO grid with a 12 km nested grid covering the Midwest. The Lake Michigan Air Directors Consortium developed the "BaseE" emissions inventory for the non-mercury species. The Wisconsin DNR developed the mercury emissions inventory and ran the MM5 meteorological model to develop the needed weather inputs. ENVIRON and AER developed all boundary and initial conditions data as well as all other model inputs. Model simulations were performed by the Wisconsin DNR.

Mercury deposition was simulated for three different meteorological scenarios; 36 km grid with the "simple-ice" mechanism, 36 km grid with Reisner ice scheme and a 36/12 km grid with the Reisner ice scheme.

The CAMx modeling results were evaluated against deposition data collected at several MDN sites in the Midwest. The evaluation showed that the modeled mercury deposition was generally higher than the observations. The Reisner ice meteorological scheme yielded deposition amounts that were a closer match to the observations than the simple-ice scheme. Model performance evaluation for CAMx needs more work. Annual/global scale modeling to date has not been adequate to describe mercury deposition processes within relatively short distance from the source. Additionally, modeling focus has been on annual runs and not episodic events. Generally, the modeling system works but it has shortcomings. These involve emissions data, cloud microphysical processes, and chemical processes.

IX. Recommendations for Future Hg Depossition Modeling

1. Conduct a more systematic model performance evaluation for both the meteorological and chemistry model output. The CAMx evaluation can be strengthened by conducting a thorough evaluation at the surface and aloft for all key gas phase and aerosol species for which observational data are available. For the mercury species, hourly, daily, and seasonal tile plots, time series plots and deposition displays should be studied to determine spatial and temporal variations in the modeled response. Since the CAMx is a new model development program there needs to be more testing, especially for episodic events.

2. Most of the speciation profiles used in mercury modeling are outdated and derived from limited sampling. The deposition models assume that most, if not all, Hg(0) leaves a regional domain during an annual run and most of Hg(II) is deposited near the source. The results of Hg deposition modeling can not be considered accurate until these profiles are validated or improved.

3. A complete MM5 model performance evaluation needs to be completed. The model developer is working on a new wet deposition technique that would be driven by surface precipitation data. Advantages with this approach are the ability to use surface rainfall amount predicted by the MM5 or interpolated observations of surface rainfall.

4. Conduct more analysis with existing data.

5. Need more resolution in monitoring data.

6. Run the model with 12 km grids placed over other areas of the Great Lakes region covering sites with available MDN data so that enough data points can be gathered to perform a statistical evaluation of performance.

7. Run the meteorological model to test different precipitation schemes to see which yields best results for wet deposition during a summertime episodic event.

X. References

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XI. Appendix A: WDNR Mercury Emissions Inventory Development

Mercury Emissions Inventory Development

Author: Grant Hetherington, WDNR

File: hg_X97579601_appA.pdf

XII. Appendix B: Environ Final Report Mercury with CAMx

Final report: Modeling atmospheric mercury chemistry and deposition with CAMx for a 2002 annual simulation.

Authors: Environ (Greg Yarwood, Steven Lau, & Yiqin Jia)
AER (Prakash Karamchandani & Krish Vijayaraghavan)

File: hg_X97579601_appB.pdf

XIII. Appendix C: Alpine Geophysics Peer Review

Scientific peer-review of the HgCAMx atmospheric mercury model and its application to the 2002 annual cycle.

Authors: Alpine Geophysics (T.W. Tesche, Dennis E. McNally, Cynthia Loomis, Gregory M. Stella, & James G. Wilkinson)

File: hg_X97579601_appC.pdf